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NONEQUILIBRIUM THERMODYNAMICS OF CONCENTRATION POLARIZATION

by

Stephen Stuart Lyman Peppin ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial

fulfillment of the requirements for the degree of Master of Science

in

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[A] model, if well made, shows at least how the universe might behave, but logical errors bring us no closer to the reality of any universe. In physical theory, mathematical rigor is of the essence.

C. Truesdell and R. Toupin, 1960

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *Nonequilibrium Thermodynamics of Concentration Polarization* submitted by Stephen Stuart Lyman Peppin in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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Abstract

Ultrafiltration is a membrane separation process with many applications, including the treating of industrial wastes and the processing of milk and juices. Academics are also interested in ultrafiltration as a possible tool for measuring empirical coefficients such as the diffusion coefficient and the permeability. One particular region of an ultrafiltration system that is not yet fully understood, and is related to a decline in the efficiency, is the concentration polarization layer, which develops as the macromolecules retained by the membrane form a highly concentrated layer that attempts to diffuse back toward the bulk of the solution. Using the postulates of classical nonequilibrium thermodynamics, a complete model, which accounts for the fact that a concentration polarization layer may have properties of both a porous medium and a region undergoing Brownian diffusion, has been derived and applied to several systems from the literature.

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Contents

Chapter 1: Introduction

1.1 Introduction 1

1.2 Thesis Goals 6

1.3 Description of the System 8

References 11

Chapter 2: Theoretical Development

2.1 Introduction 19

2.2 Balance Equations of Continuum Mechanics 20

    2.2.1 Definitions 20

    2.2.2 Mass Balance Equation 21

    2.2.3 Momentum Balance Equation 22

    2.2.4 Energy Balance Equation. 23

    2.2.5 Kinetic Energy Balance Equation 25

    2.2.6 Internal Energy Balance Equation 25

2.3 Entropy Balance Equation 26

    2.3.1 Local Equilibrium Assumption 26

    2.3.2 Definition of Internal Energy 28

    2.3.3 Entropy Balance Equation 31

2.4 Diffusive Flux. 32

2.5 Complete Theory 34

2.6 Applications 38

  2.6.1 Ordinary Diffusion 38

  2.6.2 Permeation 41

  2.6.3 Sedimentation 43

References 48

Chapter 3: Concentration Polarization

3.1 Introduction 53

3.2 Diffusive Flux 53

3.3 Complete Model of Concentration Polarization 57

References 59

Chapter 4: Literature Critique

4.1 Introduction 60

4.2 Critique of some Theories in the Literature 62

  4.2.1 Jonsson and Jonsson [1996] 62

  4.2.2 Dejmek [1975] 65

  4.2.3 Wales [1981] 66

  4.2.4 Wijmans et al. [1985] 69

  4.2.5 Johnson et al. [1987] 71

References 74

Chapter 5: Applications

5.1 Introduction 78

5.2 Bovine Serum Albumin (BSA) 78

5.2.1 Empirical Coefficient Relations.......... 79

5.2.2 BSA Ultrafiltration.......... 81

5.2.3 Kim et al.'s [1991] Permeability Prediction 85

5.2.4 Kim et al.'s [1991] Pressure Measurements 87

5.3 Hyaluronate (HA).......... 89

5.3.1 HA Ultrafiltration.......... 89

5.3.2 HA Pressure Profile.......... 93

5.3.3 Permeability Measurements of Jackson and James [1982] 97

References 114

Chapter 6: Conclusions

6.1 Conclusions 118

References 120

Appendix A: Proofs and Derivations.......... 121

Appendix B: Vector and Tensor Identities.......... 146

Appendix C: Thermodynamic Identities 153

Tables

Table 2-1 Phenomenological Coefficient Relations 46

Table A-1 Symbols (this work and **Transport Phenomena** [1960]) 122

Table A-2 Symbols (this work and **Transport Phenomena** [1960]) 126

Table A-3 Symbols (this work and **Transport Phenomena** [1960]) 130

Table A-4 Symbols (**Transport Phenomena** [1960] and **Molecular Theory of Gases and Liquids** [1964]) 132

Table A-5 Symbols (this work and Mijnlieff [1971]) 133

Table A-6 Symbols (this work and Svedberg [1940]) 137

Table A-7 Symbols (this work and Kozinski [1972]) 140

Table A-8 Symbols (this work and Tiller [1975]) 142

Figures

Figure 1-1: Dead-End Filtration System 10

Figure 5-1: Osmotic Pressure of BSA 100

Figure 5-2: Sedimentation Coefficient of BSA 101

Figure 5-3: Diffusion Coefficient of BSA 102

Figure 5-4: BSA Ultrafiltration System of Vilker et al. [1981] 104

Figure 5-5: BSA Concentration Profile 105

Figure 5-6: Permeability of BSA 106

Figure 5-7: BSA Pressure Profile. 107

Figure 5-8: HA Ultrafiltration System of Gowman [1996] 108

Figure 5-9: HA Concentration Profile 109

Figure 5-10: Diffusion Coefficient of HA 110

Figure 5-11: HA Pressure Profile. 111

Figure 5-12: HA Pressure Profile. 112

Figure 5-13: HA Pressure Profile. 113

Figure 5-14: HA Pressure Profile. 113

Notation

Boldface symbols are vectors or tensors, depending on the script (Times New Roman signifies vectors, Arial signifies tensors). Symbols that appear only in an appendix are not listed.

a	fitting parameter (used by Barry et al. [1987], Section 5.3.1)
A	flowcell cross-sectional area (used by Barry et al. [1987], Section 5.3.1)
A	flowcell cross-sectional area (used by Johnson et al. [1987], Section 4.2.5)
b	fitting parameter (used by Barry et al. [1987], Section 5.3.1)
c_k	mass fraction of the k^{th} component
c_k	density of the k^{th} component (used by Wijmans et al. [1985], Section 4.2.4)
c_p	specific heat capacity
C_2	solute concentration (used by Wales [1981], Section 4.2.3)
D	binary diffusivity/diffusion coefficient
D	binary diffusion coefficient (used by Wales [1981], Section 4.2.3)
D_q^T	phenomenological coefficient
D_1^T	phenomenological coefficient
e	specific energy (internal and kinetic)
f	friction coefficient
$\mathbf{f}^*$	friction coefficient (used by Wales [1981], Section 4.2.3)
$\mathbf{F}^*$	friction force (used by Wales [1981], Section 4.2.3)
F_{ff}	mean frictional force (used by Jonsson and Jonsson [1996], Section 4.2.1)
F_k	thermodynamic force acting on the k^{th} component (used by Wijmans et al. [1985], Section 4.2.4)
$\boldsymbol{F}_k$	body force per unit mass acting on the k^{th} component
F_{tf}	mean thermodynamic force (used by Jonsson and Jonsson [1996], Section 4.2.1)
F_1	drag force (used by Dejmek [1975], Section 4.2.2)

h_k	partial specific enthalpy of the k^{th} component
$\boldsymbol{J}_e$	internal and kinetic energy flux
J_i	mass flux of the i^{th} component (used by Wales [1981], Section 4.2.3)
$\boldsymbol{J}_k$	mass diffusive flux of the k^{th} component
$\boldsymbol{J}_{ke}$	barycentric kinetic energy flux
$\boldsymbol{J}_q$	energy flux due to conduction and diffusion
$\boldsymbol{J}_q'$	heat flux
$\boldsymbol{J}_s$	entropy flux
$\boldsymbol{J}_u$	internal energy flux
$\boldsymbol{J}_v$	momentum flux
J_v	volume flux (used by Wales [1981], Section 4.2.3)
k	permeability
ke	specific kinetic energy
ke_d	specific kinetic energy of the diffusional flows
ke_t	kinetic energy obtained by adding ke and ke_d
K	permeability (used by Johnson et al. [1987], Section 4.2.5)
l_f	concentration polarizaton layer thickness
L	phenomenological coefficient
L_p	membrane permeability (used by Vilker et al. [1981], Section 5.2.2)
L_q	phenomenological coefficient
M	mass
M_k	mass of the k^{th} component
$\hat{\boldsymbol{n}}$	outward unit normal
N'	Avogadros' number (used by Dejmek [1975], Section 4.2.2)
p	thermodynamic pressure
p_0	total driving pressure
P	pressure (used by Wijmans et al. [1985], Section 4.2.4)

P	pressure (used by Johnson et al. [1987], Section 4.2.5)
Q	volumetric flowrate (used by Barry et al. [1996], Section 5.3.1)
Q	volumetric flowrate (used by Johnson et al. [1987], Section 4.2.5)
$\boldsymbol{r}$	position vector
$\boldsymbol{r}_s$	distance from axis of rotation
s	specific entropy
$\tilde{s}$	sedimentation coefficient
s_k	partial specific entropy of the k^{th} component
S	entropy
T	temperature
u	specific internal energy
u^*	specific inner energy
U	internal energy
U	superficial solvent velocity (used by Barry et al. [1996], Section 5.3.1)
$\boldsymbol{U}$	unit tensor
U_i	velocity of the i^{th} component (used by Wales [1981], Section 4.2.3)
$\boldsymbol{v}$	barycentric velocity
$\boldsymbol{v}_{Da}$	solvent volume velocity
$\boldsymbol{v}_f$	filtrate velocity
$\boldsymbol{v}_k$	velocity of the k^{th} component
$\boldsymbol{v}^0$	mean volume velocity
V	volume
$\bar{\mathrm{V}}_{\mathrm{p}}$	solute partial molar volume (used by Dejmek [1975], Section 4.2.2)

α_p	coefficient of thermal expansion
Δp	driving pressure (used by Vilker et al. [1981], Section 5.2.2)
$\Delta \mathrm{t}$	time increment

ΔW^*	work done per unit volume
Δx	distance travelled in time Δt
$\Delta\pi$	osmotic pressure difference across the membrane (used by Vilker et al. [1981], Section 5.2.2)
η_1	solvent viscosity
μ	solvent viscosity (used by Johnson et al. [1987], Section 4.2.5)
μ_k	chemical potential of the k^{th} component
μ_k^c	concentration-dependent part of the chemical potential of the k^{th} component (used by Wijmans et al. [1985], Section 4.2.4)
μ_{p}	solute chemical potential (used by Dejmek [1975], Section 4.2.2)
μ_{p}^c	concentration-dependent part of the solute chemical potential (used by Dejmek [1975], Section 4.2.2)
π	osmotic pressure
Π	osmotic pressure (used by Johnson et al. [1987], Section 4.2.5)
ρ	total mass density
ρ_k	mass density of the k^{th} component
ρ_2^0	solute density in the bulk solution
σ	reflection coefficient (used by Vilker et al. [1981], Section 5.2.2)
σ_{ke}	rate of kinetic energy production per unit volume
σ_s	rate of entropy production per unit volume
σ_u	rate of internal energy production per unit volume
σ_v	rate of momentum production per unit volume
υ	specific volume
υ_k	partial specific volume of the k^{th} component
ω	angular velocity
Φ	dissipation function
Φ	solute volume fraction (used by Johnson et al. [1987], Section 4.2.5)

Chapter 1

Introduction

1.1 *Introduction*

Ultrafiltration is a membrane separation process in which a macromolecular solution is forced against a membrane that allows the solvent to pass through while retaining the macromolecules on the high-pressure side (see Figure 1-1). Ultrafiltration enjoys a variety of applications, including the purification of drinking water, the treating of industrial wastes, and the processing of milk and juices [Anselme, 1996; Mulder, 1996]. Academics are also interested in ultrafiltration as a possible tool for measuring empirical coefficients such as the diffusion coefficient and the permeability [Shen, 1977; Jackson, 1982; Kim, 1991; Nicolas, 1995; Barry, 1996]. As the macromolecules build up against the membrane, they form what is called a *concentration polarization layer.* It is known that the presence of a concentration polarization layer is related to a decline in the efficiency of ultrafiltration. There are three general reasons for this decline. First, the layer offers a resistance to flow in addition to the resistance of the membrane, due to the fact that the solvent must flow through the concentration polarization layer before flowing through the membrane. Second, the layer induces an osmotic pressure drop across the membrane, due to the high surface concentration, which can greatly increase the driving pressure required to maintain a constant flowrate. Third, fouling and adsorption of the solute molecules onto the membrane surface and within the pores can significantly increase the resistance of the membrane. In order to maximize the efficiency of ultrafiltration, it is important to know the role each of the three factors discussed above plays within a given system; therefore, it is important to have a sound understanding of the fluid mechanics and thermodynamics occurring within a concentration polarization layer.

Concentration polarization is not unique to ultrafiltration, however; it also occurs in reverse osmosis, where the solutes being filtered are small noninteracting particles, for example salts, and in compressible cake filtration, where the solutes are large colloids or fine clay particles. Although the basic phenomena occurring in all concentration polarization layers is essentially the same -- one component of a binary solution builds up against the membrane while the other component permeates through -- very different models have been used in the past to study reverse osmosis, cake filtration and ultrafiltration. In reverse osmosis, the layer is treated as a region undergoing ordinary diffusion [Merten, 1963; Brian, 1966]. The constitutive relation used to describe flow within the layer is Fick's law:

$$\boldsymbol{J}_2 = -\rho D \nabla c_2, \tag{1.1}$$

where $\boldsymbol{J}_2$ is the mass diffusive flux of solute, measured with respect to the mass average velocity $\boldsymbol{v}$; ρ is the total mass density of the solution; D is the binary diffusion coefficient; and, c_2 is the solute mass fraction. For steady-state reverse osmosis in dead-end filtration systems, Fick's law is sufficient to model the system. For unsteady-state reverse osmosis, Fick's law is combined with the solute mass balance to yield the convective-diffusion equation:

$$\rho \frac{\partial c_2}{\partial t} + \rho \boldsymbol{v} \cdot \nabla c_2 = \nabla \cdot \rho D \nabla c_2 . \tag{1.2}$$

Along with the relevant boundary and initial conditions, the convective-diffusion equation provides a complete model of the temporal behaviour of the system.

In cake filtration, where the solute particles are very large (relative to the particle size in reverse osmosis), it is assumed that Brownian, or Fickian, diffusion processes are negligible and the layer is treated as a porous medium [Shirato, 1969; Tiller, 1975; Tiller, 1980]. The constitutive relation used to describe flow within the layer is Darcy's law:

$$\rho_1 \upsilon_1 \boldsymbol{v}_1 = -\frac{k}{\eta_1} \nabla p , \tag{1.3}$$

or modifications of Darcy's law such as the Shirato equation:

$$\rho_1 \upsilon_1(\boldsymbol{v}_1 - \boldsymbol{v}_2) = -\frac{k}{\eta_1}\nabla p, \tag{1.4}$$

where ρ_1 is the solvent mass density; υ_1 is the solvent partial specific volume; $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ are the average velocity of the solvent and solute molecules, measured with respect to the laboratory frame; η_1 is the solvent viscosity; k is the permeability of the "porous medium"; and, p is the pressure. At steady-state, Darcy's law or the Shirato equation is sufficient to model the system. For unsteady-state filtration, it is usually combined with a mass balance.

In ultrafiltration, the solute particles are intermediate between those used in reverse osmosis and those used in cake filtration. As noted by Kozinski and Lightfoot, the concentration polarization layer of an ultrafiltration system behaves simultaneously as a porous medium and a diffusion layer [Kozinski, 1972, p1032]:

> The ultrafiltration of materials, like proteins, represents a situation intermediate between the purely diffusional behavior encountered in reverse osmosis and the purely hydrodynamic nature of ordinary filtration. . . . In reverse osmosis, the boundary layer is treated as an ideal dilute solution for which the pressure gradient will be zero. . . . In mechanical filtration, the solute is deposited or precipitates at the boundary. . . . [T]he hydrodynamic resistance of this sludge layer . . . can be obtained from conventional expressions for flow through porous media. . . . In ultrafiltration, both effects can be important since proteins in solution behave both as hydrodynamic particles of finite size and as part of the continuum. . . . [I]n concentrated solutions the pressure gradient cannot be neglected.

Kozinski and Lightfoot obtained a general constitutive relation for flow within a binary macromolecular concentration polarization layer using the Stefan-Maxwell equations of statistical mechanics; their relation contains terms related to both the concentration gradient and the pressure gradient. However, they did not obtain a complete model of macromolecular concentration polarization, capable of predicting the temporal behaviour, and they were unable to use their constitutive relation due to "insufficient thermodynamic data" [Kozinski, 1972, p1032]. Throughout the rest of their analysis, they assumed Fick's law applied within the layer, and employed the reverse osmosis model to describe their system.

Other models of ultrafiltration abound in the literature; for an extensive review of the various theories of macromolecular concentration polarization, see the paper by Bowen and Jenner [1995a]. However, no complete model of macromolecular concentration polarization, which takes into account the dual nature of the layer, has been developed. Most authors employ the reverse osmosis model, also called the osmotic pressure model, to study ultrafiltration [Michaels, 1968; Goldsmith, 1971; Kozinski, 1972; Leung, 1979; Trettin, 1981; Vilker, 1981; Wales, 1981; Clifton, 1984; Jonsson, 1984; Wijmans, 1984; Barious, 1990; Nicolas, 1995; Boulanouar, 1996; Bowen, 1996a]. The osmotic pressure model yields adequate results as long as the solute particles are relatively noninteracting, so that pressure gradients may be neglected. Others employ the cake filtration model to ultrafiltration [Jackson, 1982; Reihanian, 1983; Chudacek, 1984; McDonogh, 1984; Iritani, 1991; McDonogh, 1992; Bowen, 1995b; Bowen, 1996b; Mukai, 1997; Nakakura, 1997; Huisman, 1998]. The cake filtration model yields adequate results as long as the solute particles are quite large, so that Brownian diffusion may be neglected. Some authors have proposed combinations of the two models, for example the gel-polarization model, where it is assumed that a gel or incompressible filter cake, to which Darcy's law applies, forms on top of the membrane, and on top of the gel is a diffusion layer to which Fick's law applies [Michaels, 1968; Blatt, 1970; Porter, 1972; Dejmek, 1975; Shen, 1977; Probstein, 1978; Nakao, 1979; Trettin, 1980]. The model works in some cases; however, a distinct phase change to a gel does not always occur in macromolecular systems [Dejmek, 1975; Coniglio, 1979; Wales, 1981; Coniglio, 1982; Clark, 1986] and, although the gelling concentration should depend only on properties of the solution, the model predicts gelling concentrations which vary depending on operating conditions of the filtration system, such as the flowrate and the bulk solution concentration [Nakao, 1979; Wijmans, 1984; Aimar, 1986]. Further, and particularly for colloidal solutes, the model tends to underpredict the rate of permeate flux, sometimes by orders of magnitude [Blatt, 1970; Porter, 1972].[1]

Various other modifications and combinations exist [Nakao, 1979; Doshi, 1981; Fane, 1984; Wijmans, 1985; Aimar, 1986; Nakao, 1986; van den Berg, 1989; Nabetani, 1990; Blake, 1992; Barry, 1996; Bhattacharjee, 1996; Jonsson, 1996; Doneva, 1998]. However, none of these models allow for the fact that a macromolecular or colloidal concentration polarization layer can sustain pressure gradients and Brownian diffusion processes simultaneously. Exceptions are models using a "modified Darcy's law" [Kim, 1991; Gowman, 1997], and several force balance models [McDonogh, 1989; Petsev, 1993; Welsch, 1995; Harmant, 1996]. The modified Darcy's law is a generalization of Darcy's law in that it contains an extra term related to a concentration gradient:

$$\rho_1 \upsilon_1 \boldsymbol{v}_1 = -\frac{k}{\eta_1}(\nabla p - \nabla_T \pi), \tag{1.5}$$

where π is the osmotic pressure. The modified Darcy's law appears to be an improvement on the constitutive relation obtained by Kozinski and Lightfoot [1972], as the modified Darcy's law may be used directly, given experimental measurements or theoretical models of the permeability and the osmotic pressure. However, until recently [Elliott, 1999; this thesis, Section 3.1], no rigorous derivation of this equation was available. Also, the authors using the modified Darcy's law [Kim, 1991; Gowman, 1997] neglect the term accounting for pressure gradients, based on the results of three articles [Wales, 1981; Wijmans, 1985; Johnson, 1987] claiming to contain proofs that pressure gradients cannot exist within macromolecular concentration polarization layers.[2]

---

[1] In the gel-polarization model, it is assumed that flow is governed by Fick's law within the concentration polarization layer above the gel. Thus, the reverse osmosis model is still assumed to apply; the only difference is that the maximum concentration within the concentration polarization layer is limited by the gelling concentration of the solute. For some smaller solutes, the model yields adequate results; however, for large colloidal solutes, the model tends to severely underpredict the rate of permeate flux. It was suggested by the originators of the theory that Fick's law is not sufficient when ultrafiltering colloidal particles, and that another driving force is needed to account for the rate of permeate flux [Blatt, 1970, p74; Porter, 1972, p238]. This additional driving force could be the pressure gradient term in the generalization of Fick's law given by equation (7) of Kozinski and Lightfoot's [1972] paper or equation (3.10) of this thesis. This makes sense when we consider that, for large colloidal particles, the diffusion coefficient will approach zero as Brownian diffusion becomes negligible and the particles begin to behave like a compressible filter cake or a porous medium. The pressure gradient (Darcy's law) term in the general expression for the diffusive flux will dominate and the concentration gradient (Fick's law) term will become negligible as the solute particles approach macroscopic dimensions. Therefore, it is not surprising that using Fick's law to model such systems underpredicts the rate of permeate flux, sometimes by orders of magnitude.

Many force balance models exist in the literature [Dejmek, 1975; Wijmans, 1985; Johnson, 1987; McDonogh, 1989; Petsev, 1993; Welsch, 1995; Harmant, 1996; Jonsson, 1996]. A few of these models [McDonogh, 1989; Petsev, 1993; Welsch, 1995; Harmant, 1996] appear to obtain an expression for the mass diffusive flux which is an improvement on Kozinski and Lightfoot's equation, as the coefficients which were unknown to Kozinski and Lightfoot may be obtained in these works as functions of parameters such as ionic strength, pH and zeta-potential. However, whereas the constitutive relation in Kozinski and Lightfoot's paper was obtained by applying the boundary conditions of an ultrafiltration experiment to the Stefan-Maxwell equations of statistical mechanics, the force balances appear to be more or less intuitive constructions. Thus, the equations obtained may vary depending on the authors' interpretation of what forces should be accounted for and how. The lack of a fundamental framework, such as statistical mechanics or continuum mechanics, behind the force balance approach brings with it a danger of adding confusion to the field due to a lack of consistency and clarity regarding equations and assumptions.[3]

1.2 *Thesis Goals*

One measure of how well a particular phenomenon is understood is the number of different theories proposed to explain it. As indicated in Section 1.1, many different models of concentration polarization exist. However, the concentration polarization layer of a binary, dead-end filtration system, from a continuum point of view, is not a particularly complicated system. It contains continuous variations of pressure and concentration over macroscopic length scales, and it remains very near equilibrium over the entire duration of the filtration process. A concentration polarization layer actually provides a quintessential example of a system to which a continuum description of nature, such as classical nonequilibrium thermodynamics, should apply. The development of a complete model of concentration polarization within the general framework of nonequilibrium thermodynamics would be very useful; being a continuum theory, it

---

[2] See Chapter 4 for a review and critique of these theorems.

[3] See Chapter 4.

would describe all concentration polarization phenomena, regardless of the type of molecules involved. Differences in the physical nature of the particles within the system would by accounted for by various coefficients, such as the diffusion coefficient and the permeability, rather than by the mathematical equations describing the system. Such a model would also provide a clarifying and unifying influence on the field, as the assumptions required to obtain the model, and to reduce the model to limiting cases such as reverse osmosis and cake filtration, would be clearly enunciated. Therefore, the goals of this thesis are:

1. To obtain a complete and general model of macromolecular or colloidal concentration polarization based upon a fundamental description of a multicomponent system away from equilibrium such as nonequilibrium thermodynamics. The development should carefully record and justify all assumptions, in order to be certain of the systems to which the final results apply. The complete model should do the following:

    (a) Contain a constitutive relation accounting for the fact that a macromolecular concentration polarization layer can sustain pressure gradients and Brownian diffusion processes simultaneously.

    (b) Contain a system of differential equations capable of describing the concentration and pressure profiles within the concentration polarization layer as functions of time.

    (c) Reduce to the reverse osmosis and compressible cake filtration models as limiting cases.

2. To review some articles that have caused confusion in the literature, in an attempt to provide clarification and organization. The review should clearly state which assumptions must be made in order to use various equations found in the literature, and it should point out where mistakes have been made by authors who were unaware of the assumptions implicit in their equations.

3. To apply the complete model to some experimental systems from the literature in order to provide examples of how the model may be used directly, given currently

available experimental data, and to offer explanations for some anomalous experimental results.

The specific goals of each chapter are as follows. In Chapter 2, the equations and postulates of classical nonequilibrium thermodynamics will be used in order to obtain a fairly general model that is capable of describing several experimental situations, including ordinary diffusion, permeation and sedimentation experiments. The application of the general constitutive relation to such phenomena will be reviewed, yielding relations between various experimental coefficients. In Chapter 3, the boundary conditions of a filtration experiment will be applied to the results of Chapter 2 in order to obtain a complete model of a concentration polarization layer. In Chapter 4, a review and critique of several theorems which have caused some confusion in the literature will be given, in light of the results of Chapters 2 and 3. In Chapter 5, the concentration polarization model will be applied to various systems in the literature in order to test it and to offer explanations for some anomalous experimental results.

1.3 *Description of the System*

In general, it should be possible to use the principles of classical nonequilibrium thermodynamics to model the concentration polarization layer and membrane phase of both dead-end and cross-flow filtration systems, thereby providing a complete, continuum description of almost all filtration systems in the literature. At the present time, though, only the concentration polarization layer within dead-end filtration systems such as the one depicted in Figure 1-1 will be considered. All viscous flow, and therefore all cross-flow, is neglected. Further, the membrane phase, and any adsorption due to membrane-solute interactions, is neglected. In principle, the solution above the membrane should remain as one phase; however, for a stationary gel formed above the membrane of a dead-end ultrafiltration system (no cross-flow) it is possible that the results of this chapter are valid. If the macromolecules or colloids forming a concentration polarization layer above the membrane become highly concentrated to the point where they undergo a phase change to a gel structure or filter cake capable of elastic deformation, the Gibbs relation describing the system must account for all of the possible stress/strain relationships of the elastic medium [de Groot, 1962, p333]. However, as noted by Callen [1985, p305], "if the walls of the system impose no stress components other than the pressure, then these stress components vanish and the formalism reduces to the familiar form in which the volume is the only explicit mechanical property." Thus, the results of this chapter may apply even to a gel formed above the membrane of an ultrafiltration system, so long as the viscous stress tensor may be neglected and no shear stresses are applied to the gel (dead-end filtration with no cross-flow), and provided that properties of the phase change from a highly viscous solution to a gel are accounted for by various thermodynamic quantities such as the chemical potential. If the above conditions are met, the results of this thesis should apply to all binary concentration polarization layers formed within dead-end filtration systems, regardless of the properties of the solute molecules being filtered. Typical examples of the systems to which the model should apply are the concentration polarization layers within the filtration systems of Vilker *et al.* [1981] and Boulanouar *et al.* [1996]. Note that, in order to provide a complete description of the above systems, a model of the membrane phase, which allows for the presence of a concentration polarization layer, is required. Existing membrane transport theories assume that conditions on the membrane surface are identical to the conditions in the bulk solution [Mason, 1990; Baranowski, 1991]. It should not be difficult to extend these theories to allow for the pressure and concentration at the high-pressure side of the membrane to be controlled by the concentration polarization model, rather than by properties of the bulk solution.

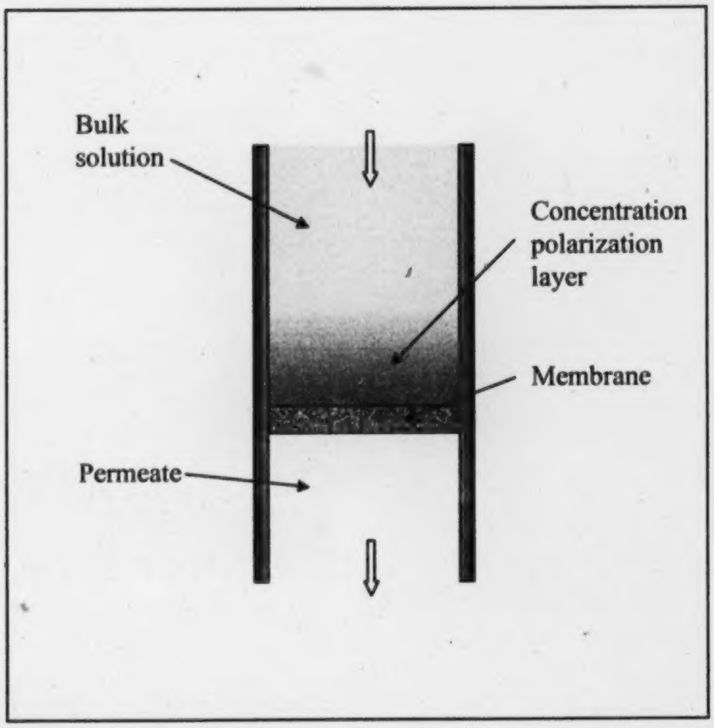
Bulk solution
Concentration polarization layer
Membrane
Permeate

Figure 1-1: Dead-end (batch) filtration system.

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Chapter 2

Theoretical Development

2.1 *Introduction*

In this chapter, our desire is to use the principles of nonequilibrium thermodynamics to derive a constitutive equation describing the diffusive flux, as well as a system of differential equations describing the temporal behaviour, within a certain class of systems which may be described as *diffusional*. In Chapter 3, our goal will be to apply this theory to the phenomenon of concentration polarization in dead-end filtration systems; therefore, we will keep track of and justify all assumptions made, in order to convince ourselves of the applicability of the final results to actual experimental systems. We will go through the derivation starting with the most fundamental equations and postulates so as to be conscious of all assumptions made along the way. The first assumption is that the system is a binary fluid which can be modelled as an isotropic, continuous medium, made up of two superposed continuous media representing the solvent and solute; therefore, our first step will be to present the multicomponent balance equations of continuum mechanics. These equations, in substantial form, describe the rates of change of mass, momentum and energy densities of a differential mass element as the centre of mass of the element moves within the continuum.

Although we will be making further assumptions along the way, the next major assumption will be that a mass element moving within the continuum is in a state of local equilibrium; we will assume that the entropy of the mass element is the same function of the local thermodynamic state as the entropy of a system in actual equilibrium. Combining this assumption with the balance equations of continuum mechanics will allow us to find a balance equation describing the rate of change of entropy density of a mass element as the centre of mass of the element moves within the continuum. This equation will contain a term describing the rate of entropy production due to irreversible processes occurring within the system. This entropy production term, at constant temperature, is the product of the mass diffusive flux and various forces (external forces and gradients in intensive variables) which cause the flux to occur; by assuming a linear relation between the flux and the driving forces appearing in the entropy production term, we will obtain a general constitutive relation for the diffusive flux in a binary system. By applying the relevant boundary conditions, this equation can be applied to many different experimental situations (diffusion experiments, sedimentation experiments, permeation experiments) to yield valuable relations between experimentally determinable parameters such as the diffusion coefficient and the permeability. The local equilibrium assumption will also allow us to convert the entropy balance equation into a balance equation describing the rate of change of the pressure within a mass element as the element moves within the continuum. Combining the pressure balance equation with the mass and momentum balance equations and the constitutive relation will yield a model capable of predicting the pressure, concentration and velocity profiles as functions of time within the system.

2.2 *Balance Equations of Continuum Mechanics*

2.2.1 *Definitions*

Throughout this derivation we will be using a Cartesian coordinate system, fixed in the laboratory frame. Boldface symbols signify vectors or tensors, depending on the script (Times New Roman signifies vectors, Arial signifies tensors). In a binary continuum the *barycentric* or centre of mass velocity $\boldsymbol{v}$ of a differential mass element is defined by the relation

$$\boldsymbol{v} = c_1\boldsymbol{v}_1 + c_2\boldsymbol{v}_2, \tag{2.6}$$

where $\boldsymbol{v}_k$ is the velocity of the centre of mass of the k^{th} continuum making up the mass element; and, c_k is the mass fraction of the k^{th} continuum making up the mass element:

$$c_k = \frac{\rho_k}{\rho}, \quad (k = 1, 2). \tag{2.7}$$

The quantity ρ_k is the mass density of the k^{th} continuum, and ρ is the total mass density:

$$\rho = \rho_1 + \rho_2 . \tag{2.8}$$

Dividing equation (2.8) by ρ and using equation (2.7) yields

$$c_1 + c_2 = 1 . \tag{2.9}$$

Next we will present the multicomponent balance equations of continuum mechanics. For a detailed derivation of these equations, see Truesdell and Toupin [1960] or Slattery [1972]; for a statistical mechanical derivation, see Irving and Kirkwood [1950] and Bearman and Kirkwood [1958] or Hirschfelder, Curtiss and Bird [1964].

2.2.2 *Mass Balance Equation*

Neglecting chemical reactions, the substantial mass balance equation for the k^{th} continuum can be written

$$\rho \frac{Dc_k}{Dt} = -\nabla \cdot \boldsymbol{J}_k, \quad (k = 1, 2), \tag{2.10}$$

where 1 refers to the solvent; 2 refers to the solute; ∇ is the del operator; $\boldsymbol{J}_k$ is the diffusive flux of component k:

$$\boldsymbol{J}_k = \rho_k(\boldsymbol{v}_k - \boldsymbol{v}), \quad (k = 1, 2); \tag{2.11}$$

and, D/Dt is the substantial derivative:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla . \tag{2.12}$$

Equation (2.10) describes the rate of change of mass fraction of component k within a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Equation (2.10) is equivalent to equation (II.13) on page 13 of

Non-Equilibrium Thermodynamics [de Groot, 1962], in the absence of chemical reactions.

The mass balance equation for the continuum as a whole, the continuity equation, may be written

$$\rho \frac{D\upsilon}{Dt} = \nabla \cdot \boldsymbol{v}, \tag{2.13}$$

where υ is the specific volume:

$$\upsilon = \rho^{-1}. \tag{2.14}$$

Equation (2.13) describes the rate of change of the specific volume within a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Equation (2.13) is equivalent to equation (II.14) on page 14 of **Non-Equilibrium Thermodynamics** [de Groot, 1962].[1]

2.2.3 *Momentum Balance Equation*

Neglecting the viscous stress tensor[2] the substantial momentum balance equation can be written

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[1] Note that equation (II.14) on page 14 of **Non-Equilibrium Thermodynamics** [de Groot, 1962] reads $\rho \frac{d\boldsymbol{v}}{dt} = \nabla \cdot \boldsymbol{v}$. This is a misprint; it should read $\rho \frac{d\upsilon}{dt} = \nabla \cdot \boldsymbol{v}$, where $\upsilon = \rho^{-1}$ is the specific volume. The error was corrected in the 1984 edition.

[2] By neglecting the viscous stress tensor, we are assuming that shear flow can be neglected and that the flow profile is flat. Mathematically, we are assuming that the viscous stress tensor does not make a significant contribution to the momentum balance equation; therefore, our analysis is restricted to systems with one dimensional "plug" flow. Such an assumption is usually made in discussions of ordinary diffusion, sedimentation and permeation [de Groot, 1962, p239; Bird, 1960, p522; Hooyman, 1953; Vink, 1961; Mijnlieff, 1971; McDonnell, 1980]. It is assumed in such experiments that flow is slow enough and steady enough that velocity gradients due to "no-slip" conditions on container walls can be neglected. In dead-end filtration experiments, the flowcell has macroscopic dimensions and flowrates are extremely small. Therefore, we will assume that the velocity is constant over a cross-section of the flowcell, and neglect the viscous term in the equation of motion. Cross-flow filtration systems, in which viscous effects must be taken into account, are not considered in this thesis.

$$\rho \frac{D\boldsymbol{v}}{Dt} = -\nabla \cdot \boldsymbol{J}_v + \boldsymbol{\sigma}_v, \tag{2.15}$$

where the tensorial flux $\boldsymbol{J}_v$, the hydrostatic pressure tensor, is given by

$$\boldsymbol{J}_v = p\boldsymbol{U}; \tag{2.16}$$

and, the vectorial production term $\boldsymbol{\sigma}_v$ is given by

$$\boldsymbol{\sigma}_v = \rho_1 \boldsymbol{F}_1 + \rho_2 \boldsymbol{F}_2. \tag{2.17}$$

The symbol p denotes the thermodynamic pressure; $\boldsymbol{U}$ is the unit tensor; and, $\boldsymbol{F}_k$ is a body force per unit mass, acting on the k^{th} component, due to external fields (gravitational, electromagnetic) or possibly due to "long-range interactions in the system" [de Groot, 1962, p15].

Equation (2.15) describes the rate of change of velocity (the acceleration) of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Combined with (2.17) and (2.16), equation (2.15) is equivalent to equation (II.19) on page 15 of **Non-Equilibrium Thermodynamics** [de Groot, 1962], in the absence of effects due to viscosity.

2.2.4 *Energy Balance Equation*

At this point we note that the energy balance equation used in **Non-Equilibrium Thermodynamics**, equation (II.28) on page 16, implicitly contains the assumption that all body forces acting within the system are conservative. We do not wish to make such an assumption, as the body force $\boldsymbol{F}_2$ postulated to exist in Section 3.2 is not conservative in general; therefore, we will use a more general energy balance, equation (18.3-3) of **Transport Phenomena** [Bird, 1960], which reduces to equation (II.28) of **Non-Equilibrium Thermodynamics** if the body forces are conservative.[3]

---

[3] See Appendix A.1 on page 121.

The substantial energy balance equation can be written

$$\rho\frac{De}{Dt} = -\nabla\cdot\boldsymbol{J}_e + \sigma_e, \tag{2.18}$$

where the energy flux $\boldsymbol{J}_e$ is given by

$$\boldsymbol{J}_e = \boldsymbol{J}_q + p\boldsymbol{U}\cdot\boldsymbol{v}. \tag{2.19}$$

The flux $\boldsymbol{J}_q$ appearing represents the energy flux due to conduction and diffusion. The energy production term σ_e is given by

$$\sigma_e = \rho_1\boldsymbol{v}_1\cdot\boldsymbol{F}_1 + \rho_2\boldsymbol{v}_2\cdot\boldsymbol{F}_2. \tag{2.20}$$

The energy per unit mass (the specific energy) e is given by

$$e = u + ke, \tag{2.21}$$

where u is the specific internal energy and ke is the specific kinetic energy[4]

$$ke = \frac{1}{2}\boldsymbol{v}^2. \tag{2.22}$$

In equation (2.22), $\boldsymbol{v}^2$ denotes $\boldsymbol{v}\cdot\boldsymbol{v}$. Equation (2.18) describes the rate of change of the specific internal and kinetic energy e of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Equation (2.18) is equivalent to equation (18.3-3) on page 560 of **Transport Phenomena** [Bird, 1960], in the absence of viscous flow.[5]

In the absence of chemical reactions and viscous effects, equations (2.10), (2.13), (2.15) and (2.18) describe the rate of change of the specific mass, momentum and energy of a mass element as the centre of mass of the element moves at the barycentric velocity within a binary continuum. Separate substantial balance equations describing the rate of change of the specific kinetic and internal energies can be found by manipulating the mass, momentum and energy balance equations, as we will see in the next sections.

---

[4] Note that some authors [Gyarmati, 1970, p69; Miyazaki, 1996, p601] feel that equations (2.21) and (2.22) are not exact because they appear to neglect the kinetic energy of diffusion. We are not in agreement with this view, but feel rather that the kinetic energy of diffusion must be included as part of u if the internal energy is to be defined correctly (see Section 2.3.2).

[5] See Appendix A.1 on page 121.

2.2.5 *Kinetic Energy Balance Equation*

To find the substantial barycentric kinetic energy balance equation, we can multiply equation (2.15), the substantial momentum balance equation, by $\boldsymbol{v}$ and use equations (2.16), (2.17), (B.14), (B.15) and (2.22) to yield

$$\rho\frac{Dke}{Dt} = -\nabla\cdot\boldsymbol{J}_{ke}+\sigma_{ke}, \tag{2.23}$$

where the kinetic energy flux $\boldsymbol{J}_{ke}$ is given by

$$\boldsymbol{J}_{ke} = p\boldsymbol{U}\cdot\boldsymbol{v}; \tag{2.24}$$

and, the kinetic energy production term σ_{ke} is given by

$$\sigma_{ke} = p\boldsymbol{U}:\nabla\boldsymbol{v}+\rho_1\boldsymbol{v}\cdot\boldsymbol{F}_1+\rho_2\boldsymbol{v}\cdot\boldsymbol{F}_2. \tag{2.25}$$

Equation (2.23) describes the rate of change of the specific barycentric kinetic energy of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Combined with (2.22), (2.24) and (2.25), equation (2.23) is equivalent to equation (II.23) on page 16 of **Non-Equilibrium Thermodynamics** [de Groot, 1962], in the absence of effects due to viscosity.

2.2.6 *Internal Energy Balance Equation*

To find the substantial internal energy balance equation, we may first insert equation (2.21) into equation (2.18) to yield

$$\rho\frac{Du}{Dt}+\rho\frac{Dke}{Dt} = -\nabla\cdot\boldsymbol{J}_e+\sigma_e. \tag{2.26}$$

Inserting equations (2.19), (2.20), (2.23), (2.24) and (2.25) into equation (2.26), and using equations (2.11) and (B.17), yields the substantial internal energy balance equation

$$\rho\frac{Du}{Dt} = -\nabla \cdot \boldsymbol{J}_u + \sigma_u, \tag{2.27}$$

where the internal energy flux $\boldsymbol{J}_u$ is given by

$$\boldsymbol{J}_u = \boldsymbol{J}_q, \tag{2.28}$$

and the internal energy production term σ_u is given by

$$\sigma_u = -p\nabla \cdot \boldsymbol{v} + \boldsymbol{J}_1 \cdot \boldsymbol{F}_1 + \boldsymbol{J}_2 \cdot \boldsymbol{F}_2. \tag{2.29}$$

Equation (2.27) describes the rate of change of the specific internal energy of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Combined with (2.28) and (2.29), equation (2.27) is equivalent to equation (II.36) on page 18 of **Non-Equilibrium Thermodynamics** [de Groot, 1962], in the absence of effects due to viscosity.

In Section 2.3, we shall write the Gibbs relation of equilibrium thermodynamics in a form that can be used, along with the balance equations of continuum mechanics, to obtain a balance equation describing the rate of change of the specific entropy of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum.

2.3 *Entropy Balance Equation*

2.3.1 *Local Equilibrium Assumption*

It is a postulate of equilibrium thermodynamics that the entropy S of a simple thermodynamic system in equilibrium is a first order homogeneous function of the internal energy U, the volume V and the masses M_k of the components.[6] Thus,

$$S = S(U, V, M_1, M_2) \tag{2.30}$$

for a binary system in equilibrium. In principle the entropy is only defined for systems in equilibrium; however, it is a postulate of ***nonequilibrium*** thermodynamics that, if a differential mass element moving at the barycentric velocity within the continuum is sufficiently near equilibrium, we may assume that the entropy of the mass element S is a first order homogeneous function of the same variables, the internal energy U, the volume V and the masses M_k, as for a system in actual equilibrium. We say that such an element is in a state of *local equilibrium.*[7] Therefore,

$$S = S(U, V, M_1, M_2) \tag{2.31}$$

for a mass element in local equilibrium.[8]

Given the local equilibrium assumption, we may apply all of the relations in Appendix C to a mass element moving at the barycentric velocity within the continuum. The first such relation we will use is the differential Gibbs relation, equation (C.9):

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{Du}{Dt} + \frac{p}{T}\frac{D\upsilon}{Dt} - \frac{\mu_1}{T}\frac{Dc_1}{Dt} - \frac{\mu_2}{T}\frac{Dc_2}{Dt}, \tag{2.32}$$

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[6] See Appendix C for a review of the thermodynamic postulates and identities used in this thesis.

[7] The concept of local equilibrium is an assumption, on the basis of which certain mathematical relations describing our system may be derived. At present, there is no *a priori* method for determining its range of validity; experiment must decide. However, this assumption generally turns out to be valid, except for systems which are very far from equilibrium [de Groot, 1962, p23]. As the systems studied in this work are not particularly far from equilibrium, we will assume that the local equilibrium assumption holds.

[8] Here, we have made the assumption that the internal energy U, the volume V and the component masses M_1, M_2 are sufficient to completely determine the entropy of a binary mass element in local equilibrium. In the most general case, the entropy may depend on other variables as well. Extended irreversible thermodynamics is the study of systems in which additional variables are required to describe the entropy; for a review of the different approaches to extended irreversible thermodynamics, see the article by Nettleton and Sobolev [1995]. In liquid systems, additional variables are generally required only for systems far removed from equilibrium. As the systems studied in this work remain quite close to equilibrium, we will assume that the independent set $\{U, V, M_1, M_2\}$ is sufficient.

where s is the specific entropy (entropy per unit mass), T is the temperature, p is the pressure, μ_k is the chemical potential of the k^{th} component[9] and u, υ and c_k are the specific internal energy, specific volume and mass fractions, as defined earlier. Equation (2.32) is equivalent to equation (III.16) on page 23 of **Non-Equilibrium Thermodynamics** [de Groot, 1962].

2.3.2 *Definition of Internal Energy*

In the literature, we have found two different definitions of the internal energy appearing in the differential Gibbs relation. In Section 2.2.4 we defined the specific internal energy by the equation

$$e = u + ke, \tag{2.33}$$

where e is the total energy per unit mass, less that due to external body forces, and ke is the kinetic energy per unit mass:

$$ke = \frac{1}{2}v^2. \tag{2.34}$$

The internal energy defined by equation (2.33) is the same as that proposed by Hirschfelder, Curtiss and Bird in the **Molecular Theory of Gases and Liquids** [1964, p654, Section 7.2e] and is used in the differential Gibbs relation of several authors discussing nonequilibrium thermodynamics [Eckart, 1940; Bird, 1955; Landau, 1959; Vink, 1961; Haase, 1962; Hirschfelder, 1964]. Several theorists, though, have suggested that the internal energy defined by equation (2.33) is not correct because the total kinetic energy per unit mass ke_t should be the summation of the specific kinetic energies of the components making up the system:

---

[9] Note that the chemical potential of the k^{th} component is defined on a mass basis in this work, whereas it is usually defined on a molar basis in thermodynamics texts [Callen, 1985, p35]. Multiplying μ_k by the molar mass $\mathcal{m}_k$ of the k^{th} component, however, yields the chemical potential as defined in Callen's book.

$$ke_t = \frac{1}{2}c_1v_1^2 + \frac{1}{2}c_2v_2^2. \tag{2.35}$$

Using equations (2.6) and (2.9), we may find the relation between ke_t and ke:

$$ke_t = ke + ke_d, \tag{2.36}$$

where ke_d is the kinetic energy per unit mass due to diffusion:[10]

$$ke_d = \frac{1}{2}c_1(v_1 - v)^2 + \frac{1}{2}c_2(v_2 - v)^2. \tag{2.37}$$

de Groot and Mazur have suggested that u is not the true internal energy because "the internal energy should contain contributions from the thermal agitation and the short-range molecular interactions" and not "the macroscopic kinetic energy of the components with respect to the centre of gravity motion" [de Groot, 1962, p28]. Rather, they argue that the true specific internal energy u^* should be defined by the relation

$$e = u^* + ke_t. \tag{2.38}$$

The internal energy defined by equation (2.38) is in agreement with the definition of several other nonequilibrium thermodynamics writers [Prigogine, 1947; Gyarmati, 1970; Slattery, 1972; Baranowski, 1991; Miyazaki, 1996]. Truesdell and Toupin [1960], in their work on continuum mechanics, thermodynamics and field theories in general, suggest that u is the correct definition of the specific internal energy [Truesdell, 1960, p613]; but, they suggest that the quantity u^*, which they call the "specific inner energy", should be used when writing the differential Gibbs relation because "any diffusion velocities, at a given place and instant, are compatible with any values of the local thermodynamic state." They suggest that "Hirschfelder, Curtiss and Bird neglect [the kinetic energy of diffusion] when they calculate [the differential Gibbs relation]" [Truesdell, 1960, p645].

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[10] Note that the kinetic energy of diffusion is often negligible with respect to the barycentric kinetic energy, making the definitions of internal energy discussed above equivalent. According to Gyarmati [1970, p54], "the kinetic energy of diffusion can in the majority of cases be neglected with respect to the barycentric kinetic energy." Fitts [1962, p26] suggests that ke_d may be neglected in all systems in which the local equilibrium assumption applies. However, within the concentration polarization layer of a dead-end filtration system at a steady state in which the solute is stationary ($v_2 = 0$), the kinetic energy of diffusion may be neglected only if the solute concentrations are low. Using equations (2.6), (2.7), (2.8), (2.34) and (2.37), we can write $ke_d/ke = c_2/c_1$. Therefore, neglecting the kinetic energy due to diffusion with respect to the barycentric kinetic energy is valid at a steady state in which the solute is stationary as long as $c_2 \ll c_1$.

In our opinion, the quantity u^* cannot be the correct definition of the specific internal energy which appears in the Gibbs relation, nor can ke_t be the correct definition of the total specific kinetic energy. Let us consider a differential mass element moving at the barycentric velocity within a binary system; we would like to define the total kinetic energy of the element. The total kinetic energy of any body is that portion of the total energy which is associated with the relative motion of the centre of mass of the body with respect to some external reference frame. The total kinetic energy of a mass element should not be a summation of the kinetic energies of the individual components within the element any more than it should be a summation of the kinetic energies of the individual molecules within the element. Further, it seems to us that the diffusion velocities are not "compatible with any values of the local thermodynamic state"; rather, they are *completely determined* by the local thermodynamic state and the local gradient of the thermodynamic state. Only the barycentric velocity is independent of, and thus compatible with, all values of the local thermodynamic state.

Let us argue on a more quantitative basis by considering the following situation. Suppose we have a box made up of two identical compartments A and B, separated by a partition. We will denote the molecules contained within compartment A as the *A molecules* and the molecules in compartment B as the *B molecules*. The pressure and temperature are held constant and no external body forces are acting on the system. When the partition is removed, the A and B molecules will interdiffuse until equilibrium is reached (the number of A molecules in each compartment is the same, and the number of B molecules in each compartment is the same). We would like to define the specific internal energy of the system during the approach to equilibrium. One possible definition is that the specific internal energy contains all of the energy per unit mass e of the diffusing molecules except for the specific kinetic energy of the components:

$$u^* = e - \frac{1}{2}c_A v_A^2 - \frac{1}{2}c_B v_B^2, \tag{2.39}$$

where c_A, c_B are the mass fractions, and v_A, v_B are the average local velocities of the A and B molecules, measured with respect to the stationary laboratory frame. Another possible definition is that the specific internal energy contains all of the energy per unit mass of the diffusing molecules except for the specific kinetic energy due to the centre of mass movement:

$$u = e - \frac{1}{2}v^2, \tag{2.40}$$

where $v = c_A v_A + c_B v_B$ is the mass average velocity.

The reason we believe that equation (2.39) defines neither the true internal energy, nor the internal energy which should be used when deriving the Gibbs relation, is because we did not say the A and B molecules and the could not be of the same type. Let us suppose that they are the same type. Even though they are the same *type* of molecules, the A molecules are a different set of molecules from the B molecules, and when the partition is removed, they are going to interdiffuse until the numbers in each compartment are the same. However, it is impossible for us to distinguish between them, and we say that the specific internal energy of the system remains constant and equal to e. Only the specific internal energy defined by equation (2.40) satisfies such a requirement; therefore, u^* cannot be the true specific internal energy.

2.3.3 *Entropy Balance Equation*

To find the substantial entropy balance equation, we may insert the substantial internal energy, specific volume and mass fraction balance equations, (2.27), (2.13) and (2.10), along with equations (2.28) and (2.29), into the Gibbs relation, equation (2.32) to yield, using also equation (B.13) and the chain rule,

$$\rho\frac{Ds}{Dt} = -\nabla \cdot \boldsymbol{J}_s + \sigma_s, \tag{2.41}$$

where the entropy flux $\boldsymbol{J}_s$ is given by

$$\boldsymbol{J}_s = \frac{1}{T}(\boldsymbol{J}_q - \mu_1\boldsymbol{J}_1 - \mu_2\boldsymbol{J}_2) \tag{2.42}$$

and the entropy production term σ_s is given by

$$\sigma_s = -\frac{1}{T^2}\boldsymbol{J}_q \cdot \nabla T - \frac{1}{T}\boldsymbol{J}_1 \cdot \left(T\nabla\frac{\mu_1}{T} - \boldsymbol{F}_1\right) - \frac{1}{T}\boldsymbol{J}_2 \cdot \left(T\nabla\frac{\mu_2}{T} - \boldsymbol{F}_2\right). \tag{2.43}$$

Equation (2.41) describes the rate of change of the specific entropy of a mass element as the centre of mass of the element moves at the barycentric velocity within the continuum. Combined with equations (2.42) and (2.43), equation (2.41) is equivalent to equation (III.19) on page 24 of **Non-Equilibrium Thermodynamics** [deGroot, 1962], in the absence of chemical reactions and effects due to viscosity. The form of the entropy production term, equation (2.43), will suggest a semi-empirical (phenomenological) constitutive relation for the diffusive flux near equilibrium in a binary system in which chemical potential gradients and external body forces exist, as we will see in the next section.

2.4 *Diffusive Flux*

The expression for the rate of entropy production per unit volume obtained in the previous section can be simplified somewhat by noting that some of the terms are not independent. In light of equation (C.66) we may write

$$\nabla\mu_k = -s_k\nabla T + \nabla_T\mu_k, \quad (k = 1, 2), \tag{2.44}$$

where s_k is the partial specific entropy of the k^{th} component and the subscript T indicates that the gradient is taken at constant temperature. Using equations (2.44) and (B.13), we may separate equation (2.43) into terms that are proportional to a temperature gradient and terms that are not:

$$\sigma_s = -\frac{1}{T^2}(J_q - h_1 J_1 - h_2 J_2) \cdot \nabla T - \frac{1}{T} J_1 \cdot (\nabla_T \mu_1 - F_1) - \frac{1}{T} J_2 \cdot (\nabla_T \mu_2 - F_2) . \quad (2.45)$$

The quantity h_k appearing in equation (2.45) is the partial specific enthalpy of the k^{th} component:

$$h_k = T s_k + \mu_k , \quad (k = 1, 2) . \quad (2.46)$$

The diffusive fluxes J_1 and J_2 are not independent. Using equations (2.11), (2.8), (2.7) and (2.6), we may write

$$J_1 + J_2 = 0 . \quad (2.47)$$

Using (2.47), equation (2.45) may be written

$$\Phi = -\frac{1}{T} J_q' \cdot \nabla T - J_1 \cdot (\nabla_T \mu_1 - \nabla_T \mu_2 - F_1 + F_2) \ , \quad (2.48)$$

where Φ, the dissipation function, is a measure of the energy dissipated within the system due to irreversible processes:

$$\Phi = T \sigma_s . \quad (2.49)$$

We have defined the heat flux J_q' by

$$J_q' = J_q - h_1 J_1 - h_2 J_2 . \quad (2.50)$$

Combined with (2.49), equation (2.48) is equivalent to equation (IV.13) on page 33 of **Non-Equilibrium Thermodynamics** [de Groot, 1962], in the absence of chemical reactions and viscous effects.

Studying equation (2.48), we see that energy is being dissipated due to conduction and diffusion phenomena. The dissipation function consists of the summation of a conductive flux J_q' multiplied by the temperature gradient, and a diffusive flux J_1 multiplied by chemical potential gradients and body forces. These gradients and forces are often called *thermodynamic forces* or *affinities* [de Groot, 1962, p25]. It is known from experiment that the presence of an affinity in a system will cause a flux, and many constitutive equations exist in the form of a flux written as a linear function of an affinity. Two examples are Fick's law of diffusion, which applies to systems in which the only affinity present is a concentration gradient, and Fourier's law of heat conduction, which applies to systems in which the only affinity present is a temperature gradient. It is also known from experiment that cross-phenomena can occur; for example, the presence of a concentration gradient can give rise to a heat flux (Dufour effect) and the presence of a temperature gradient can give rise to a diffusive flux (Soret effect). In equation (2.48), there are two independent fluxes, $\boldsymbol{J}_q'$ and $\boldsymbol{J}_1$, and two independent affinities, $-\frac{1}{T}\nabla T$ and $-(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2)$. Assuming that the fluxes and affinities appearing in the entropy production term represent the actual fluxes and affinities occurring within the system, and noting that at equilibrium all fluxes are zero, it seems reasonable, near equilibrium, to approximate the fluxes as linear functions of the affinities:

$$\boldsymbol{J}_1 = -\frac{1}{T}D_1^T\nabla T - L(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2), \tag{2.51}$$

$$\boldsymbol{J}_q' = -\frac{1}{T}D_q^T\nabla T - L_q(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2), \tag{2.52}$$

where the scalar proportionality factors D_1^T, L, D_q^T and L_q are called phenomenological coefficients. Equations (2.51) and (2.52) are general constitutive relations describing the heat and diffusion fluxes in a binary system and are equivalent to equations (IV.14) and (IV.15) on page 33 of **Non-Equilibrium Thermodynamics** [de Groot, 1962].

2.5 *Complete Theory*

In this section, we will obtain a set of differential equations that, given sufficient thermodynamic and hydrodynamic data, is capable of completely determining the temporal behaviour of our system. The independent differential equations available to us are the mass balance equations:[11]

$$\rho\frac{Dc_1}{Dt} = -\nabla\cdot\boldsymbol{J}_1, \tag{2.53}$$

and

$$\rho\frac{D\upsilon}{Dt} = \nabla\cdot\boldsymbol{v}, \tag{2.54}$$

the momentum balance equation:

$$\rho\frac{D\boldsymbol{v}}{Dt} = -\nabla p + \rho_1\boldsymbol{F}_1 + \rho_2\boldsymbol{F}_2, \tag{2.55}$$

and the entropy balance equation:

$$\rho\frac{Ds}{Dt} = -\frac{1}{T}\nabla\cdot\boldsymbol{J}_q + \frac{1}{T}\boldsymbol{J}_1\cdot\boldsymbol{F}_1 + \frac{1}{T}\boldsymbol{J}_2\cdot\boldsymbol{F}_2 + \frac{\mu_1}{T}\nabla\cdot\boldsymbol{J}_1 + \frac{\mu_2}{T}\nabla\cdot\boldsymbol{J}_2 \tag{2.56}$$

Equation (2.53) is equation (2.10); equation (2.54) is equation (2.13); equation (2.55) is equation (2.15), combined with equations (2.16), (2.17) and (B.18); and, equation (2.56) is equation (2.41), combined with equations (2.42), (2.43), (B.13) and the chain rule. These equations may be supplemented by the constitutive relations, equations (2.51) and (2.52).

Equation (2.56) is not particularly useful to us in its present form, as the entropy is difficult to work with in practical applications. However, recall that the entropy balance equation was obtained by using the differential Gibbs relation, equation (C.9), to replace the internal energy balance equation with a balance equation for the entropy. We may use a similar procedure to replace the entropy balance equation with a balance equation for the pressure. Let us choose $\{T, p, M_1, M_2\}$ as the independent variables describing the entropy rather than $\{U, V, M_1, M_2\}$.[12] This alternative functional form for the entropy yields equation (C.27), an expression analogous to the Gibbs relation:

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[11] The mass balance equations (2.10) for component 1 and 2 are equivalent; only one of them is an independent equation. This may be verified by using equations (2.9) and (2.47).

$$\frac{Ds}{Dt} = \frac{c_p}{T}\frac{DT}{Dt} - \frac{\alpha_p}{\rho}\frac{Dp}{Dt} + s_1\frac{Dc_1}{Dt} + s_2\frac{Dc_2}{Dt}, \tag{2.57}$$

where c_p is the specific heat capacity at constant pressure and α_p is the coefficient of thermal expansion. Inserting equations (2.53) and (2.56) into equation (2.57), and using equation (2.46), yields a balance equation for the pressure:

$$T\alpha_p\frac{Dp}{Dt} - \rho c_p\frac{DT}{Dt} = \nabla\cdot\boldsymbol{J}_q - \boldsymbol{J}_1\cdot\boldsymbol{F}_1 - \boldsymbol{J}_2\cdot\boldsymbol{F}_2 - h_1\nabla\cdot\boldsymbol{J}_1 - h_2\nabla\cdot\boldsymbol{J}_2. \tag{2.58}$$

Equation (2.58) is equivalent to equation (F) of Table 18.3-1 on page 562 of **Transport Phenomena** [Bird, 1960], in the absence of chemical reactions and viscous flow.[13]

Within the systems studied in this work, we will be assuming that mechanical equilibrium has been reached:[14]

$$\frac{D\boldsymbol{v}}{Dt} = 0, \tag{2.59}$$

and that the temperature remains constant and uniform:

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[12] Note that we have implicitly made this choice already in Section 2.4 by using equation (C.66).

[13] See Appendix A.2 on page 125.

[14] By assuming the system has reached mechanical equilibrium, we are assuming that barycentric accelerations within the system are small. We do not assume these accelerations are zero, because the concentration polarization layers of the filtration systems studied in this work will rearrange themselves over time, causing accelerations to occur. However, we are assuming that the acceleration term in the momentum balance equation (2.55) can be neglected with respect to the pressure gradient and the external body forces. de Groot notes that "in the cases of diffusion or thermal diffusion in closed vessels one can safely assume that a state of mechanical equilibrium . . . is quickly realized to a sufficient approximation" [de Groot, 1962, p44]. de Groot was considering only ordinary diffusion experiments and not filtration, or forced diffusion, experiments; however, Haase [1969, p230] points out that in "slow processes such as diffusion, heat conduction, slow chemical reactions, etc., . . . 'local mechanical equilibrium', i.e. the disappearance of the barycentric acceleration, is approximately satisfied, corresponding to the neglection of inertial forces." Given the low flowrates used in most dead-end filtration experiments, we will assume that barycentric accelerations and inertial forces may be neglected.

$$\frac{DT}{Dt} = 0, \quad \nabla T = 0. \tag{2.60}$$

Under these conditions, our system of independent equations, (2.53), (2.54), (2.55) and (2.58), may be written

$$\rho\frac{Dc_1}{Dt} = -\nabla \cdot \boldsymbol{J}_1, \tag{2.61}$$

$$\rho\frac{D\upsilon}{Dt} = \nabla \cdot \boldsymbol{v}, \tag{2.62}$$

$$0 = -\nabla p + \rho_1 \boldsymbol{F}_1 + \rho_2 \boldsymbol{F}_2, \tag{2.63}$$

$$T\alpha_p \frac{Dp}{Dt} = \nabla \cdot \boldsymbol{J}_q' + \boldsymbol{J}_1 \cdot (\nabla_T h_1 - \nabla_T h_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2). \tag{2.64}$$

Also, the constitutive relations (2.51) and (2.52) reduce to

$$\boldsymbol{J}_1 = -L(\nabla_T \mu_1 - \nabla_T \mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2), \tag{2.65}$$

$$\boldsymbol{J}_q' = -L_q(\nabla_T \mu_1 - \nabla_T \mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2). \tag{2.66}$$

Equation (2.64) was obtained by combining equations (2.50), (2.60), (B.13) and (2.47) with equation (2.58). Equations (2.61) through (2.66) may be used to model the behaviour of any system satisfying the following assumptions.

In deriving the above set of differential equations we have assumed that the system is a fluid which can be modelled as an isotropic continuum (page 19). We have neglected chemical reactions (page 21) and viscous flow (page 22). Further, we assumed that we can apply equilibrium thermodynamical concepts to a mass element in local equilibrium as the element moves within the continuum (page 26), and we assumed that the system is sufficiently near equilibrium that we can write the diffusive flux as a linear function of the affinities (page 34). Finally, we assumed that mechanical equilibrium has been reached and that the temperature is constant (page 36).

Equation (2.65), or an equivalent expression, has been used to study ordinary diffusion, sedimentation and permeation experiments [Onsager, 1932; deGroot, 1952;

Hooyman, 1953; Vink, 1961; Mijnlieff, 1971; McDonnell, 1980]. In the next few sections, we will review how nonequilibrium thermodynamics has been applied to the above experimental situations as this will yield useful relations between the phenomenological coefficient L, the diffusion coefficient D, the sedimentation coefficient $\tilde{s}$ and the permeation coefficient k.

2.6 *Applications*

2.6.1 *Ordinary Diffusion*

This section follows the discussion of ordinary diffusion given by Hooyman, Holton, Mazur and de Groot [1953]. In ordinary diffusion experiments performed to measure diffusion coefficients, it is assumed, in addition to the assumptions summarized after equation (2.65), that there are negligible body forces acting on the system:

$$\boldsymbol{F}_k = 0, \quad (k = 1, 2). \tag{2.67}$$

Using equation (2.67), we see that the momentum balance equation (2.63) reduces to

$$\nabla p = 0. \tag{2.68}$$

Using equations (2.68) and (2.67), we see that the expression for the diffusive flux, equation (2.65), reduces to

$$\boldsymbol{J}_1 = -L(\nabla_{T,p}\mu_1 - \nabla_{T,p}\mu_2), \tag{2.69}$$

where the subscripts T and p indicate that the gradient is taken at constant temperature and pressure. At constant temperature and pressure, the Gibbs-Duhem relation, equation (C.38), may be written

$$\rho_1 \nabla_{T,p}\mu_1 + \rho_2 \nabla_{T,p}\mu_2 = 0; \tag{2.70}$$

therefore, equation (2.69) becomes, using also equation (2.7),

$$\boldsymbol{J}_1 = -\frac{L}{c_2}\nabla_{T,p}\mu_1. \tag{2.71}$$

Thus, in an ordinary diffusion experiment, the diffusive flux is a linear function of the constant temperature and pressure chemical potential gradient.

In a binary system at constant temperature and pressure, a chemical potential gradient may be written, using equation (C.66),

$$\nabla_{T,p}\mu_1 = \left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}\nabla c_1 . \tag{2.72}$$

Inserting equation (2.72) into (2.71) yields

$$\boldsymbol{J}_1 = -\frac{L}{c_2}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}\nabla c_1 . \tag{2.73}$$

Fick's law, an empirical expression which describes flow in systems undergoing ordinary diffusion, may be written [Hooyman, 1953, p1104, equation (66)]

$$\boldsymbol{J}_1 = -\rho D\nabla c_1 , \tag{2.74}$$

where D is the diffusion coefficient (diffusivity). Comparing equation (2.73) with (2.74) yields a relation between the phenomenological coefficient and the diffusion coefficient:

$$L = c_2\rho\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}^{-1} D . \tag{2.75}$$

Equation (2.75) is equivalent to equation (72) on page 1105 of the paper by Hooyman *et al.* [1953].[15]

Note that, by using equation (2.75), we can write the general expression for the diffusive flux, equation (2.65), in terms of the more familiar diffusion coefficient rather than the phenomenological coefficient:

$$\boldsymbol{J}_1 = -c_2\rho\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}^{-1} D(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2) . \tag{2.76}$$

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[15] See Appendix A.3 on page 127.

Equation (2.76) is equivalent to equation (18.4-14), a general expression for the diffusive flux in a binary system given on page 568 of **Transport Phenomena** [Bird, 1960], in the absence of temperature gradients.[16]

Sometimes friction coefficients are used to describe ordinary diffusion experiments rather than diffusion coefficients. A binary friction coefficient f may be defined by a relation of the form [Lamm, 1957; Laity, 1959; Bearman, 1961]

$$f(\boldsymbol{v}_1 - \boldsymbol{v}_2) = -\rho_1 \nabla_{T,p}\mu_1 . \tag{2.77}$$

Let us find a relation between f and L. Using equations (2.6) and (2.9), equation (2.11) may be written, for component 1,

$$\boldsymbol{J}_1 = \rho_1 c_2(\boldsymbol{v}_1 - \boldsymbol{v}_2). \tag{2.78}$$

Thus, equation (2.71) may be written

$$\rho_1 c_2(\boldsymbol{v}_1 - \boldsymbol{v}_2) = -\frac{L}{c_2}\nabla_{T,p}\mu_1 . \tag{2.79}$$

Comparing equation (2.79) with equation (2.77) yields a relation between the friction coefficient f and the phenomenological coefficient L:

$$L = \frac{(\rho_1 c_2)^2}{f}. \tag{2.80}$$

Note that, by using equations (2.80) and (2.78), equation (2.65) may be written in the form of a force balance:

$$f(\boldsymbol{v}_1 - \boldsymbol{v}_2) = -\rho_1 c_2(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2). \tag{2.81}$$

Equation (2.81) is equivalent to equation (18.4-14) of **Transport Phenomena** [Bird, 1960], in the absence of temperature gradients.[17] The left hand side of equation (2.81) may be interpreted as a frictional force and the right hand side is the opposing thermodynamic force in a system satisfying the assumptions summarized after equation (2.65). Equations (2.76) and (2.81) are two equivalent expressions for the diffusive flux; using equation (2.78), these equations may be combined to yield a relation between the friction coefficient and the diffusion coefficient:

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[16] See Appendix A.4 on page 127.

[17] See Appendix A.4 on page 127.

$$D = \frac{\rho_1 c_1 c_2}{f}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}. \tag{2.82}$$

2.6.2 *Permeation*

This section follows the discussions of permeation given by Vink [1961], Mijnlieff and Jaspers [1970], and McDonnell and Jamieson [1980]. In the nonequilibrium thermodynamical treatment of permeation, the membrane is thought to be a component of the continuum, for example component 2, and the permeate is component 1. It is assumed that component 2 is held in place,

$$\boldsymbol{v}_2 = 0, \tag{2.83}$$

and at uniform concentration,

$$\nabla c_2 = 0, \tag{2.84}$$

by a suitable body force $\boldsymbol{F}_2$. Negligible body forces act on the permeate:

$$\boldsymbol{F}_1 = 0. \tag{2.85}$$

Using equation (2.85), the momentum balance equation (2.63) reduces to

$$\boldsymbol{F}_2 = \frac{\nabla p}{\rho_2}. \tag{2.86}$$

Using equations (2.86), (2.85), (2.84), (2.83) and (2.78), the general expression for the diffusive flux, equation (2.65), reduces to

$$\boldsymbol{J}_1 = c_2 \rho_1 \boldsymbol{v}_1 = -L\left(\nabla_{T,c_2}\mu_1 - \nabla_{T,c_2}\mu_2 + \frac{\nabla p}{\rho_2}\right), \tag{2.87}$$

where the subscripts T and c_2 indicate that the gradient is taken at constant temperature and concentration. At constant temperature and concentration, the Gibbs-Duhem relation (C.38) may be written, in light of (2.9),

$$\rho_1 \nabla_{T,c_2}\mu_1 + \rho_2 \nabla_{T,c_2}\mu_2 = \nabla p. \tag{2.88}$$

Therefore, equation (2.87) may be written, using equations (2.88), (2.7) and (2.8),

$$\boldsymbol{J}_1 = c_2 \rho_1 \boldsymbol{v}_1 = -\frac{L}{c_2}\nabla_{T,c_2}\mu_1. \tag{2.89}$$

Thus, in a permeation experiment, the diffusive flux is a linear function of the constant temperature and concentration chemical potential gradient. In a binary system with uniform temperature and concentration, a chemical potential gradient may be written, using equation (C.66),

$$\nabla_{T,c_2}\mu_1 = \upsilon_1 \nabla p, \tag{2.90}$$

where υ_1 is the partial specific volume of component 1. By inserting equation (2.90), equation (2.89) can be written

$$\rho_1 \upsilon_1 \boldsymbol{v}_1 = -L\left(\frac{\upsilon_1}{c_2}\right)^2 \nabla p. \tag{2.91}$$

Darcy's law, an empirical expression describing flow in porous media, can be written [Mijnlieff, 1971, p1841, equation (13)][18]

$$\rho_1 \upsilon_1 \boldsymbol{v}_1 = -\frac{k}{\eta_1}\nabla p, \tag{2.92}$$

where k is the permeation coefficient (permeability) of the solute molecules and η_1 is the viscosity of the solvent. Comparing equations (2.91) and (2.92) yields a relation between the phenomenological coefficient and the permeability:

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[18] Note that equation (13) of the paper by Mijnlieff and Jaspers [1971] is missing a minus sign. It is simply a misprint, though, and does not affect the rest of their paper.

$$L = \left(\frac{c_2}{\upsilon_1}\right)^2 \frac{k}{\eta_1}. \tag{2.93}$$

Equation (2.93) is equivalent to equation (14) on page 1841 of the paper by Mijnlieff and Jaspers [1971].[19]

Combining equations (2.75) and (2.93) yields an expression relating D to k:

$$D = \frac{c_2}{\rho \upsilon_1^2}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \frac{k}{\eta_1}. \tag{2.94}$$

2.6.3 *Sedimentation*

In this section we will follow the discussions of sedimentation given by Mijnlieff and Jaspers [1971] and Hooyman, Holton, Mazur and de Groot [1953]. We will be studying that portion of a sedimenting fluid in which concentration gradients are zero:

$$\nabla c_2 = 0. \tag{2.95}$$

In the nonequilibrium thermodynamical treatment of sedimentation, it is assumed that the body forces $\boldsymbol{F}_1$ and $\boldsymbol{F}_2$ are both equal to the centrifugal force per unit mass acting on the system:

$$\boldsymbol{F}_k = \omega^2 \boldsymbol{r}_s, \quad (k = 1, 2), \tag{2.96}$$

where ω is the angular velocity of the system and $\boldsymbol{r}_s$ is the distance from the axis of rotation.

Using equations (2.96) and (2.8), the momentum balance equation (2.63) reduces to

$$\nabla p = \rho \omega^2 \boldsymbol{r}_s. \tag{2.97}$$

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[19] See Appendix A.5 on page 133.

Using equations (2.96) and (2.95), the general expression for the diffusive flux, equation (2.65), reduces to

$$J_1 = -L\cdot(\nabla_{T,c_2}\mu_1 - \nabla_{T,c_2}\mu_2), \tag{2.98}$$

where the subscripts T and c_2 indicate that the gradient is taken at constant temperature and concentration. At constant temperature and concentration, the Gibbs-Duhem relation (C.38) may be written, in light of (2.9),

$$\rho_1\nabla_{T,c_2}\mu_1 + \rho_2\nabla_{T,c_2}\mu_2 = \nabla p; \tag{2.99}$$

therefore, equation (2.98) can be written, using also equations (2.8) and (2.7),

$$J_1 = -\frac{L}{c_1}\left(\frac{\nabla p}{\rho} - \nabla_{T,c_2}\mu_2\right). \tag{2.100}$$

In a binary system at constant temperature and concentration, the solute chemical potential gradient can be written, analogously to equation (2.90),

$$\nabla_{T,c_2}\mu_2 = \upsilon_2\nabla p. \tag{2.101}$$

Inserting (2.101) into (2.100) yields, using also equation (2.97),

$$J_1 = -\frac{L}{c_1}(1-\rho\upsilon_2)\omega^2 r_s. \tag{2.102}$$

It is assumed in sedimentation experiments that the mean volume velocity v^0, defined by

$$v^0 = \rho_1\upsilon_1 v_1 + \rho_2\upsilon_2 v_2, \tag{2.103}$$

is negligible [Hooyman, 1953, p1106]. Therefore, v_1 and v_2 are related:

$$v_1 = -\frac{\rho_2\upsilon_2}{\rho_1\upsilon_1}v_2. \tag{2.104}$$

Inserting equation (2.104) into (2.78), and using equation (C.56), the diffusive flux $\boldsymbol{J}_1$ may be written

$$\boldsymbol{J}_1 = -\frac{c_2}{\upsilon_1}\tilde{s}\omega^2\boldsymbol{r}_s, \tag{2.105}$$

where the sedimentation coefficient $\tilde{s}$ is defined by

$$\tilde{s} = \frac{\boldsymbol{v}_2}{\omega^2\boldsymbol{r}_s}. \tag{2.106}$$

Inserting equation (2.105) into equation (2.102) yields a relation between the phenomenological coefficient and the sedimentation coefficient

$$L = \frac{c_1c_2}{\upsilon_1(1-\rho\upsilon_2)}\tilde{s}. \tag{2.107}$$

Equation (2.107) is equivalent to equation (12) on page 1840 of the paper by Mijnlieff and Jaspers [1971].[20]

Combining equations (2.107) and (2.93) yields, using (2.7),

$$k = \frac{\rho_1\upsilon_1\eta_1}{\rho_2(1-\rho\upsilon_2)}\tilde{s}. \tag{2.108}$$

Using equations (C.56) and (2.8), we may write

$$(1-\rho\upsilon_2) = \rho_1(\upsilon_1-\upsilon_2). \tag{2.109}$$

Inserting (2.109) into (2.108) yields a relation between the permeability k and the sedimentation coefficient $\tilde{s}$:

$$k = \frac{\eta_1\tilde{s}}{\rho_2(1-\upsilon_2/\upsilon_1)}. \tag{2.110}$$

---

[20] See Appendix A.6 on page 134.

Equation (2.110) is equivalent to equation (15) of the paper by Mijnlieff and Jaspers [1971], and is frequently used to estimate the permeability from measurements of the sedimentation coefficient [Ethier, 1986; Comper, 1989; Kim, 1991]. Combining equations (2.107) and (2.75) yields a relation between the diffusion coefficient D and the sedimentation coefficient $\tilde{s}$:

$$D = \frac{c_1}{\rho\upsilon_1(1-\rho\upsilon_2)}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}\tilde{s}. \tag{2.111}$$

For very dilute macromolecular solutions, equation (2.111) reduces to the Svedberg equation of sedimentation.[21]

The results of Sections 2.6.1 through 2.6.3 are summarized in Table 2-1. All of the entries in the table are equivalent to the phenomenological coefficient L; thus, any two entries can be combined to obtain a relation between the two corresponding empirical coefficients. The bottom row indicates the page at which each of the relationships to L were presented.

Table 2-1 Phenomenological Coefficient Relations

Phenomenological Coefficient (L)	**Diffusion Coefficient (D)**	**Friction Coefficient (f)**	**Permeation Coefficient (k)**	**Sedimentation Coefficient ($\tilde{s}$)**
L (1)	$c_2\rho\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p}^{-1}D$ (2)	$\frac{(\rho_1 c_2)^2}{f}$ (3)	$\left(\frac{c_2}{\upsilon_1}\right)^2\frac{k}{\eta_1}$ (4)	$\frac{c_1 c_2}{\upsilon_1(1-\rho\upsilon_2)}\tilde{s}$ (5)
	page 39	page 40	page 43	page 45

By applying the appropriate boundary conditions to equation (2.65), and by comparing the resulting expression with the appropriate constitutive equation, we have found relations between the phenomenological coefficient L, the diffusion coefficient D, the friction coefficient f, the permeability k and the sedimentation coefficient $\tilde{s}$.

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[21] See Appendix A.7 on page 135.

The procedure used in Sections 2.6.1 through 2.6.3 may analogously be used to find relations between D, f, k or $\tilde{s}$ and any other coefficient for which an empirical constitutive equation exists to describe flow in a system satisfying the assumptions summarized after equation (2.65). Such relations are quite useful because accurate measurements of any one of these coefficients, for example the sedimentation coefficient, will in principle allow one to calculate all of the other coefficients. Experimental tests of these relations have been performed by several groups [Phillies, 1976; Wijmans, 1985; Comper, 1986]. In Chapter 5 we will test the relation between the sedimentation coefficient and the diffusion coefficient using experimental data for the protein bovine serum albumin (BSA).

In Chapter 2, we have obtained a complete model which is capable, in principle, of describing any system satisfying the assumptions summarized after equation (2.65). In Chapter 3, we will make some further assumptions allowing us to obtain a complete model of a concentration polarization layer within a dead-end filtration system. Given the relevant boundary and initial conditions, and provided that experimental measurements or theoretical models of the necessary thermodynamic and hydrodynamic coefficients are available, this model will be capable of describing the temporal behaviour of any concentration polarization layer, regardless of the physicochemical properties of the solute molecules.

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Chapter 3

Concentration Polarization

3.1 *Introduction*

In this chapter, we will use the results of Chapter 2 in order to study the phenomenon of concentration polarization in dead-end filtration systems. Our model will only apply to binary concentration polarization layers formed above the membrane of bulk filtration systems; we will neither attempt to analyse cross-flow filtration systems, nor the membrane phase of dead-end filtration systems, nor any adsorption layers which arise due to membrane-solute interactions. The model could conceivably be extended to account for the above phenomena; however, such a generalization is beyond this thesis, as it would require a three component system with viscous flow taken into account.

3.2 *Diffusive Flux*

In this section, we will apply the boundary conditions of a dead-end filtration experiment to the general constitutive relation, equation (2.65), and use the relations obtained in Sections 2.6.1 through 2.6.3, in order to obtain a constitutive relation capable of describing flow within a binary concentration polarization layer. We will assume, in addition to the assumptions summarized after equation (2.66), that any body forces acting on the solvent are negligible (gravitational effects are not significant in ultrafiltration):

$$\boldsymbol{F}_1 = 0. \tag{3.1}$$

However, as noted by Kozinski and Lightfoot [1972], the solute molecules in the concentration polarization layer may "transmit a body force from the membrane," causing $\boldsymbol{F}_2$ to be non-zero. Using equation (3.1), the momentum balance equation (2.63) reduces to

$$\rho_2 \boldsymbol{F}_2 = \nabla p. \tag{3.2}$$

Using equations (3.2) and (3.1), the general constitutive relations (2.65) and (2.66) may be written

$$\boldsymbol{J}_1 = -L\left(\nabla_T\mu_1 - \nabla_T\mu_2 + \frac{\nabla p}{\rho_2}\right), \tag{3.3}$$

$$\boldsymbol{J}_q' = -L_q\left(\nabla_T\mu_1 - \nabla_T\mu_2 + \frac{\nabla p}{\rho_2}\right), \tag{3.4}$$

where the subscript T indicates that the gradient is taken at constant temperature. At constant temperature, the Gibbs-Duhem relation (C.38) may be written

$$\rho_1 \nabla_T\mu_1 + \rho_2 \nabla_T\mu_2 = \nabla p; \tag{3.5}$$

therefore, equations (3.3) and (3.4) become, using also equations (2.8) and (2.7),

$$\boldsymbol{J}_1 = -\frac{L}{c_2}\nabla_T\mu_1, \tag{3.6}$$

$$\boldsymbol{J}_q' = -\frac{L_q}{c_2}\nabla_T\mu_1. \tag{3.7}$$

Thus, the diffusive flux $\boldsymbol{J}_1$ and the heat flux $\boldsymbol{J}_q'$ within an isothermal concentration polarization layer are linear functions of the constant temperature chemical potential gradient. Equation (3.6) is equivalent to equation (7) of the 1972 paper by Kozinski and Lightfoot.[1] Kozinski and Lightfoot were unable to use equation (7) of their paper due to a lack of experimental data for the phenomenological coefficient; therefore, during the rest of their analysis, they neglected pressure gradients within the concentration polarization layer. In the following paragraphs of this section, we will show how equation (3.6) may be written in several forms that are directly usable, given thermodynamic and hydrodynamic data currently available in the literature.

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[1] See Appendix A.8 on page 137.

Equation (3.6) can be written in several more useful and meaningful forms by employing the relations summarized in Table 2-1; we will derive three different forms below, although many others are possible. We will write equation (3.6) in terms of the diffusion coefficient D and the permeability k first, as this will be beneficial from a conceptual point of view. In a binary system at constant temperature, a chemical potential gradient can be written, using equation (C.66),

$$\nabla_T \mu_1 = \upsilon_1 \nabla p + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \nabla c_1 . \tag{3.8}$$

Inserting equation (3.8) into equation (3.6) yields

$$J_1 = -\frac{L}{c_2}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \nabla c_1 - L\left(\frac{\upsilon_1}{c_2}\right)\nabla p . \tag{3.9}$$

Now we may use the equations relating L to D and L to k that we obtained while studying ordinary diffusion and permeation. Inserting entries (2) and (4) of Table 2-1 into equation (3.9) yields an expression which reduces to Fick's law in the absence of pressure gradients, and to Darcy's law for a stationary solute with no concentration gradients:

$$J_1 = -\rho D \nabla c_1 - \frac{c_2}{\upsilon_1}\frac{k}{\eta_1}\nabla p . \tag{3.10}$$

Equation (3.10) is very appealing conceptually in that it reflects the fact that a macromolecular or colloidal concentration polarization layer has properties of both a region undergoing ordinary diffusion and a porous medium. Note that, if the concentration polarization layer contains solute particles that are large enough for Brownian, or Fickian, diffusion processes to be neglected (for example fine clay particles or large colloids), but still contains concentration (porosity) gradients, equation (3.10) reduces to the Shirato equation of compressible cake filtration [Shirato, 1969; Tiller, 1975; Nakakura, 1997].[2]

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[2] See Appendix A.9 on page 141.

We can alternatively write equation (3.6) in terms of the permeability and the osmotic pressure gradient. Using equation (C.97), the constant temperature chemical potential gradient may be written

$$\nabla_T \mu_1 = \upsilon_1 \nabla p - \upsilon_1 \nabla_T \pi, \tag{3.11}$$

where π is the osmotic pressure of the solvent. Inserting equation (3.11) into equation (3.6) yields

$$\boldsymbol{J}_1 = -L\left(\frac{\upsilon_1}{c_2}\right)(\nabla p - \nabla_T \pi). \tag{3.12}$$

Inserting entry (4) of Table 2-1 into equation (3.12) yields another possible form of equation (3.6), written in terms of the permeability and the osmotic pressure gradient:

$$\boldsymbol{J}_1 = -\left(\frac{c_2}{\upsilon_1}\right)\frac{k}{\eta_1}(\nabla p - \nabla_T \pi). \tag{3.13}$$

Note that, if the system has reached a steady state in which the solute is stationary ($\boldsymbol{v}_2 = 0$), equation (3.13) may be written, using equations (2.11), (2.6) and (2.9),

$$\boldsymbol{v}_{Da} = -\frac{k}{\eta_1}(\nabla p - \nabla_T \pi), \tag{3.14}$$

where $\boldsymbol{v}_{Da}$ is the volume velocity of the solvent moving through the stationary solute:

$$\boldsymbol{v}_{Da} = \rho_1 \upsilon_1 \boldsymbol{v}_1 . \tag{3.15}$$

Equation (3.14) has been used before to study flow within macromolecular concentration polarization layers and is called the *modified Darcy's law* [Kim, 1991; Gowman, 1997]. Equation (3.13), then, is a generalization of the modified Darcy's law to systems in which the solute may be moving. As we will see in Section 5.2.3, some anomalous results obtained while studying an ultrafiltration system of bovine serum albumin (BSA) [Kim, 1991] can be explained by the fact that the modified Darcy's law was used within a system in which the solute was not stationary.

Although equations (3.10) and (3.13) are very appealing forms of equation (3.6), in that equation (3.10) is a combination of Fick's law and Darcy's law, and equation (3.13) is a generalization of the modified Darcy's law, accurate measurements of the permeability or the diffusion coefficient of macromolecules in solution are difficult to obtain; therefore, it will be beneficial to look at one more possible form of equation (3.6). Perhaps the easiest of the coefficients in Table 2-1 to measure is the sedimentation coefficient $\tilde{s}$. Thus, from an experimental point of view, we would like to write equation (3.6) in terms of $\tilde{s}$. Inserting entry (5) of Table 2-1 into equation (3.12), and using equations (C.56), (2.8), (2.7) and (2.14), yields a constitutive relation for the diffusive flux in a binary, macromolecular concentration polarization layer, written in terms of the sedimentation coefficient:

$$\boldsymbol{J}_1 = -\frac{\upsilon}{\upsilon_1 - \upsilon_2}\tilde{s}(\nabla p - \nabla_T \pi) . \tag{3.16}$$

3.3 *Complete Model of Concentration Polarization*

In Section 3.2 we obtained a constitutive relation, equation (3.10), applicable within the concentration polarization layer of a dead-end filtration system, by assuming, in addition to the assumptions summarized after equation (2.66), that $\boldsymbol{F}_1$ is zero, but that a non-zero body force $\boldsymbol{F}_2$ arises within the system due to the restraining force exerted by the membrane. The balance equations describing our system, (2.61) through (2.64), may now be combined to yield

$$\rho\frac{Dc_1}{Dt} = -\nabla \cdot \boldsymbol{J}_1 , \tag{3.17}$$

$$\rho\frac{D\upsilon}{Dt} = \nabla \cdot \boldsymbol{v} , \tag{3.18}$$

$$T\alpha_p\frac{Dp}{Dt} = \nabla \cdot \boldsymbol{J}_q' + \boldsymbol{J}_1 \cdot \left(\nabla_T h_1 - \nabla_T h_2 + \frac{1}{\rho_2}\nabla p\right). \tag{3.19}$$

These equations may be supplemented by the constitutive relations (3.10) and (3.7),

$$J_1 = -\rho D\nabla c_1 - \frac{c_2}{\upsilon_1}\frac{k}{\eta_1}\nabla p, \tag{3.20}$$

$$J_q' = -\frac{L_q}{c_2}\nabla_T\mu_1. \tag{3.21}$$

Given the relevant boundary and initial conditions, along with experimental measurements or theoretical models of the necessary hydrodynamic and thermodynamic coefficients, equations (3.17) through (3.21) should, in principle, be capable of completely describing the temporal behaviour of any binary concentration polarization layer within a dead-end filtration system, regardless of the physicochemical properties of the solute molecules. Such a concentration polarization layer must, however, satisfy the assumptions summarized after equation (2.66) (cross-flow systems and adsorption layers cannot be modelled by the above equations). At present, equations (3.17) through (3.21) are quite complex and are not in a form that is suitable for direct experimental use.[3] It may be possible to considerably simplify the above system using the fact that the density is often considered constant in ultrafiltration systems [Trettin, 1980; Vilker, 1981; Gowman, 1996], and that the Dufour effect is often negligible ($L_q = 0$), at least within liquid systems [Bird, 1955, p77; Bird, 1960, p566; de Groot, 1962, p279]. However, further analysis is required. Note that, within systems in which the pressure and density may be considered constant, and in which the Dufour effect is negligible, equations (3.17) through (3.21), along with (2.12), (2.9) and (2.7), reduce to the familiar convective-diffusion equation:

$$\frac{\partial\rho_2}{\partial t} + \boldsymbol{v}\cdot\nabla\rho_2 = \nabla\cdot D\nabla\rho_2. \tag{3.22}$$

This completes our analysis of concentration polarization. In Chapter 5 we will attempt to apply some of what we have learned to actual experimental systems.

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[3] Except for equation (3.20), see Section 5.3.2. In order to obtain a complete and useable model of an experimental ultrafiltration system, a description of the membrane phase in the presence of a concentration polarization layer is also required. It should not be too difficult to extend existing theories of membrane transport [Mason, 1990; Baranowski, 1991] to allow for the presence of a concentration polarization layer above the membrane (see Section 5.2.2).

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Chapter 4

Literature Critique

4.1 *Introduction*

As we discussed in Chapter 1, a macromolecular or colloidal concentration polarization layer has properties of both a region undergoing ordinary diffusion and a porous medium. Thus, pressure gradients and concentration gradients can be maintained within the system at the same time. Further, since pressure gradients and concentration gradients are independent driving forces for diffusive flow, a constitutive relation describing flow within a macromolecular concentration polarization layer should contain terms related to both gradients. The above sentiments were articulated quite clearly by Kozinski and Lightfoot in 1972. "The ultrafiltration of materials, like proteins, represents a situation intermediate between the purely diffusional behaviour encountered in reverse osmosis and the purely hydrodynamic nature of ordinary filtration. . . . [I]n concentrated solutions the pressure gradient cannot be neglected" [Kozinski, 1972, p1032]. In Section 3.1 we made certain assumptions allowing us to derive a constitutive relation applicable within a macromolecular concentration polarization layer; Kozinski and Lightfoot, in the first part of their 1972 paper, make essentially the same assumptions:

> 1. In reverse osmosis, the boundary layer is treated as an ideal dilute solution for which the pressure gradient will be zero. [The general constitutive relation describing flow] then simplifies to the familiar form of Fick's law for a binary solution.
>
> 2. In mechanical filtration, the solute is deposited or precipitates at the boundary. These restrained solutes can now transmit an equivalent body force from the supported membrane. In addition, the gradient in chemical potential approaches zero as the solute becomes totally immobilized. The coefficient of the pressure gradient is now the hydrodynamic resistance of this sludge layer and can be obtained from conventional expressions for flow through porous media.

> 3. In ultrafiltration, both effects can be important since proteins in solution behave both as hydrodynamic particles of finite size and as part of the continuum. At low levels of polarization, chemical potentials predominate as in reverse osmosis. At high levels of polarization the protein precipitates or gels and hydrodynamic potentials predominate as in ordinary filtration.
>
> The most interesting condition is that of highly concentrated solutions which have not gelled. The protein molecules may still to a degree transmit a body force from the membrane, but the chemical potential gradient is not zero.

Note that when Kozinski and Lightfoot use the phrase "chemical potential" they are speaking of the concentration-dependent part of the chemical potential only (essentially the osmotic pressure). Hence the statement, "the gradient in chemical potential approaches zero as the solute becomes totally immobilized," refers only to the osmotic pressure gradient. The total chemical potential gradient would not be zero in such a situation as it contains a term related to the pressure gradient.[1]

Kozinski and Lightfoot were unable to use their general expression for the diffusive flux, due to "insufficient thermodynamic data." Instead, they assumed ordinary Fickian diffusion throughout the rest of their paper. Almost all subsequent analyses of macromolecular concentration polarization either assume from the beginning that the layer is a region undergoing "purely diffusional behavior" and employ Fick's law or that the layer is a region undergoing "mechanical filtration" and employ Darcy's law. For an extensive review of the various theories of macromolecular concentration polarization, see the paper by Bowen and Jenner [1995a].

Most theories assume *a priori* that either Fick's law or Darcy's law may be applied within the layer; however, several theorists have published papers claiming to prove that the pressure is constant within macromolecular concentration polarization layers [Wales, 1981; Wijmans, 1985; Johnson, 1987]. The end result has been considerable uncertainty concerning what assumptions or equations may or may not be applied when modelling a macromolecular concentration polarization layer. In this chapter, we will first take a look at a recent paper which exemplifies the present state of confusion [Jonsson, 1996], and then show how the one basic mistake made in that paper -- realizing that the pressure likely varies within macromolecular concentration polarization layers, but using equations that are only valid within constant pressure systems -- can also explain why several authors came to the conclusion that pressure gradients are zero.

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[1] See Section C.4 on page 161.

4.2 *Critique of some Theories in the Literature*

4.2.1 *Jonsson and Jonsson [1996]*

The main goal of Jonsson and Jonsson's paper is to derive an expression for the steady state diffusive flux within a binary, colloidal concentration polarization layer by performing a force balance. "Concentrating on a single particle, the force balance gives

$$F_{ff} = F_{tf} \tag{4.1}$$

where F_{ff} is the mean frictional force and F_{tf} is the mean thermodynamic force on the particle" [Jonsson, 1996, p506]. That such a force balance should exist within the layer at steady state seems reasonable. However, problems arise when one attempts to determine the form for F_{ff} and F_{tf}. The frictional force is relatively straightforward; one may assume that, for low velocities, F_{ff} is a linear function of the velocity difference between the solute and solvent. Determining the appropriate thermodynamic force, though, is more difficult. Jonsson and Jonsson, following Atkins [1990, p761], suggest that the proper thermodynamic force is the constant temperature and pressure chemical potential gradient, essentially the osmotic pressure gradient. But Atkins clearly states that such a form for the thermodynamic force is only valid within systems at constant temperature and pressure. So, by proposing such a thermodynamic force, Jonsson and Jonsson are implicitly assuming that pressure gradients and temperature gradients are zero within colloidal concentration polarization layers. This is the main mistake of their paper, as there is no reason to assume that the pressure is constant; in fact, Jonsson and Jonsson suggest that the pressure should drop across "stable, very concentrated" layers [Jonsson, 1996, p507] and entire theories of colloidal concentration polarization have been developed under the assumption that Darcy's law applies within the layer [Reihanian, 1983; Chudacek, 1984; McDonogh, 1984; Iritani, 1991; McDonogh, 1992; Bowen, 1995b; Bowen, 1996b; Mukai, 1997; Nakakura, 1997; Huisman, 1998]. As we will see later, all of the authors attempting to prove that pressure gradients are zero in macromolecular concentration polarization layers make a similar mistake at some point in their derivation.

Before continuing on, we note that Jonsson and Jonsson incorrectly suggest that their force balance is a generalization of Fick's law. "A serious shortcoming of [Fick's law] is that the diffusive flow is written as $(-DdC/dx)$. This representation of the diffusive flow can be used only for solutions with noninteracting solutes (i.e., ideal solutions)" [Jonsson, 1996, p505]. The above statement is not correct, as D is in general a function of concentration, and Fick's law accurately describes the diffusive flow in nonideal systems as long as external body forces are absent and the temperature and pressure are constant [Bird, 1960, Chapter 16]. Within ideal solutions, the diffusive flux would be written, in Jonsson and Jonsson's notation, $(-D_0 dC/dx)$, where D_0 is the diffusion coefficient at the dilute limit. "In colloidal dispersions, with long-range interactions between the colloidal particles in the dispersion, the diffusive flow is proportional to . . . the derivative of the chemical potential of the particles" [Jonsson, 1996, p505]. Certainly the above statement is correct; however, within binary systems at constant temperature and pressure, it is no more than an alternative statement of Fick's law. When discussing the work of Wijmans, Nakao, van den Berg, Troelstra and Smolders [1985], Jonsson and Jonsson erroneously state that Wijmans *et al.*, who assumed that Fick's law applied within their system, made the "assumption that the mass transfer due to diffusion only depends on the concentration gradient and not on the gradient of the chemical potential" [Jonsson, 1996, p505]. Since Jonsson and Jonsson assume constant temperature and pressure in their equations, the two assumptions they are attempting to distinguish are, in fact, the same assumption. When Jonsson and Jonsson use the phrase "chemical potential" they are, similarly to Kozinski and Lightfoot [1972], considering only the concentration-dependent part of the chemical potential; therefore, when they suggest that flow is a linear function of the "derivative of the chemical potential," they are also suggesting that flow is a linear function of the concentration gradient, and the result is not a generalization of Fick's law; it is a completely equivalent statement. This equivalence has been recognized by many authors and the result is a "generalized Stokes-Einstein" equation, which relates the diffusion coefficient appearing in Fick's law to the concentration-dependent part of the chemical potential (or, alternatively, the osmotic pressure or the activity coefficient) within a concentrated solution [Onsager, 1932, p2759; Wijmans, 1985, p123; Bowen, 1998, p162; this thesis, Section 2.6.1 and equation (2.94)].

When performing a force balance in the boundary layer of a macromolecular or colloidal filtration system, it is very important to ensure that the correct form of the thermodynamic force is used. One way to unequivocally obtain this force is to study the dissipation function $\Phi = T\sigma_s$, which is a measure of the total energy being dissipated per unit volume within the concentration polarization layer. As we saw in Section 2.4, the dissipation function, in the most general case, consists of the summation of the fluxes within the system multiplied by the thermodynamic forces or affinities causing the fluxes to occur. Therefore, assuming a linear relation between the fluxes and thermodynamic forces appearing in Φ should yield, near equilibrium, the correct form for the force balance. Such a force balance is given by equation (2.81) or, equivalently, by equation (11.2-54) of the **Molecular Theory of Gases and Liquids** [Hirschfelder, 1964],[2] sometimes called the Stefan-Maxwell equation [Bird, 1960, p570; Lightfoot, 1962].

That the above equations represent a force balance was recognized by Scattergood and Lightfoot in 1968. "Each term on the left side of [the Stefan-Maxwell] equation represents a molar force tending to move species *i* relative to the others and each term on the right a "frictional" interaction or "drag" proportional to this relative motion" [Scattergood, 1968, p1136]. Once such a general force balance has been obtained, one may then apply the boundary conditions of a diffusion, permeation, sedimentation or filtration experiment, as we saw in Sections 2.6.1 to 2.6.3 and Section 3.1, to reduce the equation into simpler forms that apply to each particular situation. The safest method, then, is to start with the general force balance and then determine which assumptions may be applied to simplify the equation. This is the approach to macromolecular concentration polarization taken in Kozinski and Lightfoot's 1972 paper. Choosing the thermodynamic force thought to exist on a more or less intuitive basis, as was done in Jonsson and Jonsson's 1996 paper, can lead to confusion and error.

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[2] See Appendix A.4 on page 127.

4.2.2 *Dejmek [1975]*

Dejmek's thesis contains an early attempt at describing a macromolecular concentration polarization layer through the use of a force balance. Although Dejmek never came to the conclusion that pressure gradients are zero, most authors who did modelled their approach after his; therefore, we will discuss Dejmek's work first. Section 5.2 of Dejmek's thesis is called "The Force Balance in the Boundary Layer." In it, Dejmek discusses the force balance that must exist at steady state within a concentration polarization layer [Dejmek, 1975, p57]:

> The forces acting on a stationary particle must be balanced. In this case, the forces are the gradient of [the] chemical potential and the hydrodynamic drag force on the particle (gravitational force is neglected), Hartley and Crank, 1949.
>
> $$\frac{d\mu_p}{dx} = F_1 N' \qquad (4.2)$$
>
> [where] F_1 [is the] drag on one particle and N' [is] Avogadros' number.

Dejmek is evidently following the force balance approach given by Hartley and Crank in Section 8 of their discussion on ordinary diffusion [Hartley, 1949, p815]. The most general force balance given in Hartley and Crank's paper, though, is between a hydrodynamic drag force and the gradient of the concentration dependent part of the chemical potential (written in terms of activity coefficients) [Hartley, 1949, p817]. Thus, the force balance in Hartley and Crank's paper, and therefore equation (4.2), is only valid in systems at constant temperature and pressure, as was recognized by Bearman [1961]. However, Dejmek writes [1975, p57]

> In [the] absence of [an] electric field, and at constant temperature, only pressure and concentration contribute to the potential gradient
>
> $$\bar{V}_p \frac{dp}{dx} + \frac{d\mu_p^c}{dx} = F_1 N' \tag{4.3}$$
>
> [where] $\bar{V}_p$ [is the] partial molar volume of solute and $d\mu_p^c$ signifies variations of the concentration dependent part of the chemical potential of the solute.

Thus, similarly to Jonsson and Jonsson [1996], Dejmek suspects that pressure gradients exist within macromolecular concentration polarization layers, but then attempts to employ a force balance, equation (4.2), that is only valid in constant pressure systems. As we will see in the next sections, it is a similar error which has led three different authors to the conclusion that pressure gradients are zero.

4.2.3 *Wales [1981]*

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Wales is interested in obtaining an expression for the pressure profile within a binary concentration polarization layer of an ultrafiltration system. He attempts to perform an energy balance on his system; however, as with Jonsson and Jonsson in 1996 and with Dejmek in 1975, Wales employs an equation in his derivation that is only valid within systems at constant pressure. Wales begins by defining $\mathbf{F}^*$ as the force per unit volume acting on component 1 due to the relative motion of the two components. If the system is sufficiently near equilibrium, we may assume that $\mathbf{F}^*$ is a linear function of the velocity difference $(\boldsymbol{v}_1 - \boldsymbol{v}_2)$:

$$\mathbf{F}^* = f^*(\boldsymbol{v}_1 - \boldsymbol{v}_2), \tag{4.4}$$

where f^* may be thought of as a type of friction coefficient and is equivalent to the friction coefficient defined in Section 2.6.1 of this work:

$$f^* = f. \tag{4.5}$$

Equation (4.4) is equivalent to equation (1) of Wales' paper. During a time increment Δt, the work done (per unit volume) by $\mathbf{F}^*$ is

$$\Delta W^* = \mathbf{F}^* \cdot \Delta \mathbf{x}, \tag{4.6}$$

where $\Delta \mathbf{x}$ is the distance component 1 travelled relative to component 2 in time Δt:

$$\Delta \mathbf{x} = (\boldsymbol{v}_1 - \boldsymbol{v}_2)\Delta t. \tag{4.7}$$

Assuming the only work done on the system is that due to the diffusional flows (*i.e.* neglecting chemical reactions, temperature gradients and viscous flow), the total rate of energy dissipation per unit volume Φ may be written

$$\Phi = \lim_{\Delta t \to 0} \frac{\Delta W^*}{\Delta t}; \tag{4.8}$$

or, using (4.4), (4.6) and (4.7),

$$\Phi = f^*(\boldsymbol{v}_1 - \boldsymbol{v}_2)^2 \tag{4.9}$$

where $(\boldsymbol{v}_1 - \boldsymbol{v}_2)^2$ denotes $(\boldsymbol{v}_1 - \boldsymbol{v}_2) \cdot (\boldsymbol{v}_1 - \boldsymbol{v}_2)$. Equation (4.9) is equivalent to equation (2) of Wales' paper.

Thus, Wales realizes that a safe way to determine the thermodynamic force in opposition to the frictional force in a macromolecular concentration polarization layer is to study the dissipation function Φ, which is given by equation (3) of his paper:

$$\Phi = -\sum_i J_i \frac{d\mu_i}{dx}, \tag{4.10}$$

where J_i is the molar flux of the i^{th} component and μ_i is the chemical potential (defined on a molar basis) of the i^{th} component. Unfortunately, Wales does not derive the above equation himself; rather, he obtains it from Chapter 9 of **Nonequilibrium Thermodynamics in Biophysics** by Katchalsky and Curran [1965]. The problem is that Katchalsky and Curran derive their expression for the dissipation function while working under the assumption of uniform pressure, as they show quite clearly in Section 7.4 on page 82 of their work. They also neglect external forces, viscous effects and assume mechanical equilibrium.[3] Therefore, the energy balance given in Wales' paper cannot be used to obtain an expression for the pressure gradient because it already contains the assumption of uniform pressure. In our notation, equation (3) of Wales' paper is, for a binary system,

$$\Phi = -\rho_1 \boldsymbol{v}_1 \cdot \nabla_{T,p}\mu_1 - \rho_2 \boldsymbol{v}_2 \cdot \nabla_{T,p}\mu_2 . \tag{4.11}$$

The dissipation function Wales should have used is equation (IV.13) of **Nonequilibrium Thermodynamics** [de Groot, 1962] or equation (2.48) of this work. Equation (2.48) may be written, under isothermal conditions,

$$\Phi = -\boldsymbol{J}_1 \cdot (\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2) . \tag{4.12}$$

Equation (4.12) reduces to equation (4.11) only if body forces are absent and the pressure is constant.[4]

Before finishing our discussion of Wales' paper, we note that Wales combines equations (2) and (3) of his paper and then uses the Gibbs-Duhem equation, along with some other thermodynamic identities, to yield equation (15) of his paper:

$$\frac{dp}{dx} = \frac{1}{D}\frac{d\pi}{dC_2}\left(1 - \frac{J_2}{C_2 J_v}\right)\left(D\frac{\partial C_2}{\partial x} - C_2(U_1 - U_2)\right), \tag{4.13}$$

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[3] Note that, although Katchalsky and Curran [1965] neglect external body forces and pressure gradients in their derivation in Chapter 7, in Chapter 9 they use their dissipation function to study sedimentation in a centrifugal field in which pressure gradients exist. This is only valid because the external force is conservative and the system is in mechanical equilibrium, in which case the more general dissipation function given by equation (IV.13) of **Nonequilibrium Thermodynamics** [de Groot, 1962], or equation (2.48) of this work, reduces to Katchalsky and Curran's. The chemical potential used by Katchalsky and Curran in such cases has been modified to include the potential associated with the conservative body force. Such a modification is not possible in ultrafiltration, though, as the body force acting on the solute is not conservative in general.

[4] See Appendix A.10 on page 142.

where p is the pressure, D is the diffusion coefficient, π is the osmotic pressure, C_2 is the solute concentration, J_v is the volume flux and U_i is the velocity of the i^{th} component. Wales then asserts that the quantity in the second brackets of (4.13) is zero:

$$D\frac{\partial C_2}{\partial x} - C_2(U_1 - U_2) = 0. \tag{4.14}$$

Thus, Wales assumes that equation (4.14), essentially Fick's law (if solute concentrations are low), is valid within the concentration polarization layer and combines equations (4.13) and (4.14) to obtain the result

$$\frac{dp}{dx} = 0. \tag{4.15}$$

However, equation (4.14) is not valid, because Fick's law may only be used within systems in which the pressure is known to be uniform [Bird, 1960, p502, footnote 1, see also p564]. In fact, had Wales used the correct dissipation function in equation (3) of his paper, then, after combining with equation (2) and using the Gibbs-Duhem equation and the other thermodynamic identities, equation (15) of his paper would have been a generalization of Fick's law to systems in which pressure gradients exist.[5]

4.2.4 *Wijmans* et al. *[1985]*

As discussed in the previous section, Wales in 1981 attempted to prove that pressure gradients are zero in ultrafiltration concentration polarization layers through the use of an energy balance. Wijmans, Nakao, van den Berg, Troelstra and Smolders attempt to prove the same thing in 1985 by using a force balance. As we will see, Wijmans *et al.* make essentially the same mistake as Wales, in that the force balance used by Wijmans *et al.* is only valid within systems at constant pressure, and therefore cannot be used to derive an expression for the pressure gradient. In the section "Force Balance in the Boundary Layer" of their paper, Wijmans *et al.* suggest that there are certain forces, F_0 and F_1, acting on the solvent and solute, respectively, of a binary concentration polarization layer. Equation (8) of their paper,

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[5] For example, combining equations (4.12) and (4.9), and using equations (4.5) and (2.78), yields equation (2.81), a general expression for the diffusive flux that is equivalent to equation (18.4-14) of **Transport Phenomena** [Bird, 1960], in the absence of temperature gradients.

$$c_0F_0 + c_1F_1 = 0, \tag{4.16}$$

is a force balance assumed to exist between F_0 and F_1 at steady-state, where c_i is the density of the i^{th} component. Certainly equation (4.16) may be valid, provided that the correct expressions are used for F_0 and F_1. Wijmans *et al.* suggest the following forms:

$$F_0 = \frac{\mathrm{d}\mu_0}{\mathrm{d}x} = \frac{\mathrm{d}\mu_0^c}{\mathrm{d}x} + \upsilon_0\frac{\mathrm{d}P}{\mathrm{d}x}, \tag{4.17}$$

$$F_1 = \frac{\mathrm{d}\mu_1}{\mathrm{d}x} = \frac{\mathrm{d}\mu_1^c}{\mathrm{d}x} + \upsilon_1\frac{\mathrm{d}P}{\mathrm{d}x}, \tag{4.18}$$

where μ_i is the chemical potential of the i^{th} component, μ_i^c is the concentration-dependent part of the chemical potential and υ_i is the partial specific volume of the i^{th} component. Inserting equations (4.17) and (4.18) into (4.16) yields

$$c_0\frac{\mathrm{d}\mu_0}{\mathrm{d}x} + c_1\frac{\mathrm{d}\mu_1}{\mathrm{d}x} = 0. \tag{4.19}$$

No argument explaining why equations (4.17) and (4.18) are the correct expressions for F_0 and F_1 is given by Wijmans *et al.*; rather, these equations appear to be intuitive assumptions. Wijmans *et al.* suggest that the force balance given by equation (4.19) is valid as long as "the complete boundary layer has the properties of a Newtonian fluid" [Wijmans, 1985, p120]. We fail to see why such a condition is a necessary requirement. In fact, it can be shown quite readily that the necessary requirement for the validity of equation (4.19) is that the system be at constant pressure. The constant temperature Gibbs-Duhem equation may be written, in Wijmans *et al.*'s notation,

$$c_0\frac{\mathrm{d}\mu_0}{\mathrm{d}x}+c_1\frac{\mathrm{d}\mu_1}{\mathrm{d}x} = \frac{\mathrm{d}P}{\mathrm{d}x}. \tag{4.20}$$

The Gibbs-Duhem equation is a fundamental relation of the thermodynamics of simple systems; assuming that the local equilibrium assumption holds, we may be confident that equation (4.20) is valid. Only when the pressure is constant does the Gibbs-Duhem equation reduce to (4.19); therefore, the necessary requirement for the validity of the force balance suggested by Wijmans *et al.* is that the pressure be constant. Thus, Wijmans *et al.*, in accordance with Jonsson and Jonsson in 1996, Dejmek in 1975 and Wales in 1981, realize that pressure gradients likely exist within ultrafiltration concentration polarization layers, but then employ an equation which is only valid within constant pressure systems. Wijmans *et al.*'s proof consists of assuming the validity of both their force balance and the Gibbs-Duhem equation, and then comparing these two equations to obtain the result

$$\frac{\mathrm{d}P}{\mathrm{d}x} = 0. \tag{4.21}$$

However, since the force balance of Wijmans *et al.* is *only valid at constant pressure*, it cannot be used to obtain (4.21).

4.2.5 *Johnson* et al. *[1987]*

Johnson, Kamm, Ethier and Pedley's attempt to prove that pressure gradients are zero in macromolecular concentration polarization layers is the most recent of which we are aware. In conformance with all previous attempts, Johnson *et al.* employ an equation that is only valid at constant pressure in their attempt to prove that pressure gradients are zero. Johnson *et al.* are considering a binary concentration polarization layer at a steady state in which the solute molecules are stationary. They suggest on page 435, equation (19), that "a modified Darcy's law" may be used to describe flow within the layer:

$$\frac{\mathrm{d}}{\mathrm{dx}}(\mathrm{P}-\Pi) = \frac{\mu \mathrm{Q}}{\mathrm{KA}}, \tag{4.22}$$

where P is the pressure, Π is the osmotic pressure, μ is the solvent viscosity, K is the permeability, Q is the volumetric flowrate and A is the cross-sectional area of the flowcell. We are in complete agreement with such an assumption, as a main result of this thesis is a derivation showing that, if the solute molecules are stationary, the modified Darcy's law is the constitutive equation that should be used to describe flow within the concentration polarization layer.[6]

Johnson *et al.* then suggest that the following force balance, equation (20) of their paper, also applies within the layer:

$$\frac{d}{dx}(\Pi) = -\frac{\mu Q}{KA}. \tag{4.23}$$

Johnson *et al.* do not derive or reference their equations (19) and (20), but appear to state them on an intuitive basis. Equation (4.23) is not a separate force balance, but is simply equation (4.22) without the pressure gradient term. That equation (4.23) neglects pressure gradients can be seen by using equation (17) of Johnson *et al.*'s paper, the generalized Stokes-Einstein equation (valid in the form given by Johnson *et al.* only for low solute concentrations):

$$D = \frac{K\Phi}{\mu}\frac{d\Pi}{d\Phi}, \tag{4.24}$$

where Φ is the solute volume fraction. Equation (4.23) may be rearranged and written in the form

$$\frac{Q}{A} = -\frac{K}{\mu}\frac{d\Pi}{d\Phi}\frac{d\Phi}{dx}. \tag{4.25}$$

Combining equations (4.24) and (4.25) yields

$$\Phi\frac{Q}{A} = -D\frac{d\Phi}{dx}. \tag{4.26}$$

---

[6] See Section 3.1.

Equation (4.26) is Fick's law (within a system in which the solute concentrations are low and the solute is stationary); therefore, since Fick's law only applies to systems at constant pressure [Bird, 1960, p502, footnote 1; see also p564], equations (4.26) and (4.23) neglect pressure gradients. Johnson *et al.*'s proof consists of assuming the validity of both equations (4.22) and (4.23), and then comparing these two equations to obtain the result

$$\frac{dP}{dx} = 0. \tag{4.27}$$

However, since equation (4.23) is *only valid in the absence of pressure gradients*, their proof has no meaning.

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Chapter 5

Applications

5.1 *Introduction*

In Chapter 3, we used the postulates of nonequilibrium thermodynamics to obtain a complete model of a binary concentration polarization layer within a dead-end filtration system. Ideally, we would now like to test our model by predicting the pressure, concentration and velocity profiles as functions of time within one or more systems from the literature and then comparing with experimental measurements. Unfortunately, we have not yet been able to make any reliable predictions as the model is still quite complex and experimental data for all of the necessary coefficients is not available. In this chapter, then, we will simply point out some systems in which pressure gradients likely exist. Other goals of this chapter are to test the relations between the empirical coefficients obtained in Sections 2.6.1, 2.6.2 and 2.6.3, and to offer explanations for some anomalous experimental and theoretical results from the literature.

5.2 *Bovine Serum Albumin (BSA)*

In this section, we will first test the relation between the diffusion coefficient and the sedimentation coefficient obtained in Section 2.6.3 using data for the protein bovine serum albumin (BSA). Then we will discuss the models of BSA concentration polarization used by Vilker, Colton and Smith [1981], Boulanouar, Nicolas and Bariou [1996] and Bowen and Williams [1996b] to predict their experimental measurements, as they provide examples of the different viewpoints which have been employed to explain macromolecular concentration polarization. Finally, we will review the analysis of Vilker *et al.*'s experiments given by Kim, Wang, Johnson and Kamm [1991], in order to explain some anomalous results obtained in that paper.

5.2.1 *Empirical Coefficient Relations*

In this section we will test the relation between the diffusion coefficient D and the sedimentation coefficient $\tilde{s}$, obtained in Section 2.6.3 and summarized in Table 2-1, for the protein bovine serum albumin (BSA). Tests of this type have been done before [Phillies, 1976; Wik, 1982; Wijmans, 1985; Comper, 1986] yielding, for the most part, quite satisfying results, given the difficulties inherent in making accurate measurements of such coefficients. We will only test the relation between D and $\tilde{s}$ because measurements of the other coefficients in Table 2-1, particularly k, are difficult to perform[1] and we were unable to find much experimental data on them.

Combining entries (2) and (5) of Table 2-1 yields a relation between D and $\tilde{s}$:

$$D = \frac{c_1}{\rho \upsilon_1 (1 - \rho \upsilon_2)} \left(\frac{\partial \mu_1}{\partial c_1} \right)_{T,p} \tilde{s} . \qquad (5.1)$$

Given that equation (5.1) reduces to the Svedberg equation of ultracentrifugation for dilute macromolecular solutions,[2] we suspect that it is a valid relation; however, there are adequate experimental measurements of D and $\tilde{s}$ available, so we will test it. During experimental measurements of sedimentation coefficients and diffusion coefficients, the solute concentrations are kept low enough to assume that ρ is approximately constant; therefore, equation (5.1) may be written, using equations (2.9) and (2.7),

$$D = \frac{-\rho_1}{\rho \upsilon_1 (1 - \rho \upsilon_2)} \left(\frac{\partial \mu_1}{\partial \rho_2} \right)_{T,p} \tilde{s} . \qquad (5.2)$$

Before testing equation (5.2), we should write it in terms of the osmotic pressure π, rather than the chemical potential μ_1, as π is the quantity usually measured in experiments. Differentiating equation (C.96) with respect to ρ_2, while holding T and p constant, yields

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[1] See Section 5.3.3.

[2] See Appendix A.7 on page 135.

$$\left(\frac{\partial\mu_1}{\partial\rho_2}\right)_{T,p} = -\upsilon_1\left(\frac{\partial\pi}{\partial\rho_2}\right)_T. \tag{5.3}$$

Inserting equations (5.3), (2.109) and (2.14) into equation (5.2) yields

$$D = \frac{\upsilon}{\upsilon_1-\upsilon_2}\left(\frac{\partial\pi}{\partial\rho_2}\right)_T\tilde{s}. \tag{5.4}$$

Scatchard *et al.* [1944] and Kim *et al.* [1991] measured the osmotic pressure of BSA as a function of concentration; their data is plotted on Figure 5-1. There appears to be fairly good agreement between the measurements. Scatchard *et al.* used $0.15M$ NaCl as the solvent, pH 7.4, 25^0 C; Kim *et al.* used an NaCl solution of unspecified ionic strength as the solvent, pH 7.3, unspecified temperature. Also shown on Figure 5-1 is a fit of the data using a second order polynomial:

$$\pi = (0.00156+0.196\rho_2+5.90\rho_2^2)\times10^6, \quad \left(\frac{dyne}{cm^2}\right), \tag{5.5}$$

with ρ_2 in units of g/cm^3. van den Berg [1989] and Comper [1989] measured the sedimentation coefficient of BSA as a function of concentration; their data is plotted on Figure 5-2. The agreement between the sedimentation coefficient measurements is not as good. van den Berg used $0.125M$ NaCl as the solvent, pH 7.4, 20^0 C; Comper used $0.15M$ NaCl as the solvent, pH 7.5, 20^0 C. Also shown on Figure 5-2 is a fit of the data using a second order polynomial:

$$\frac{1}{\tilde{s}} = (0.0223+0.213\rho_2+1.07\rho_2^2)\times10^{14}, \quad \left(\frac{1}{s}\right). \tag{5.6}$$

The partial specific volume υ_2 of BSA remains constant over a wide concentration range [Vilker, 1981, p642]; we will use the value of $0.730cm^3/g$ given by Comper

[1989, p129]. Since the solutions are fairly dilute, we will use the values of pure water for υ_1 and υ.

The diffusion coefficient predicted using equations (5.4), (5.5) and (5.6) is plotted on Figure 5-3, along with experimental measurements of the diffusion coefficient using light scattering and ultracentrifuge techniques made by Phillies, Benedek and Mazer [1976] (0.15*M* NaCl, pH 7.4, 25^0 C), Fair, Chao and Jamieson [1978] (0.13*M* NaCl, pH 7.4, 22^0 C) and van den Berg and Smolders [1989] (0.1*M* NaCl, pH 7.4, 20^0 C). Equation (5.4) has been able to predict the order of magnitude of the diffusion coefficient of BSA. Given that the data for π, $\tilde{s}$ and D were obtained by several different authors using different batches of BSA under varying conditions, we feel that the fit is quite acceptable. Perhaps more extensive measurements of $\tilde{s}$, taken using 0.15*M* rather than 0.125*M* ionic conditions, would yield a better prediction. Note that Bowen, Mongruel and Williams [1996a] and Bowen and Mongruel [1998], using a theoretical model of the osmotic pressure, performed a similar test on BSA. Their prediction is in agreement with ours, in that it overpredicts the experimental measurements of the diffusion coefficient somewhat.

5.2.2 *BSA Ultrafiltration*

In 1981, Vilker, Colton and Smith measured the permeate flux and the concentration profile within a polarization layer containing 0.15*M* NaCl as the solvent and bovine serum albumin (BSA) as the solute (see Figures 5-4 and 5-5). Vilker *et al.* used a membrane that was highly rejecting to BSA (rejection coefficient >0.99 [Vilker, 1981, p642]) and also highly resistant to adsorption and fouling. Vilker *et al.* assumed that Fick's law applied within their system (therefore, they neglected pressure gradients):

$$J_2 = -\rho D \nabla c_2. \tag{5.7}$$

The mass balance equation (2.10), written for component 2, is

$$\rho \frac{Dc_2}{Dt} = -\nabla \cdot \boldsymbol{J}_2. \tag{5.8}$$

Combining equations (5.7) and (5.8), and using equation (2.12), yields the convective-diffusion equation:

$$\rho \frac{\partial c_2}{\partial t} + \rho \boldsymbol{v} \cdot \nabla c_2 = \nabla \cdot \rho D \nabla c_2. \tag{5.9}$$

Vilker *et al.* [1981, p639] assumed that ρ and D were approximately constant in their system. Thus, for the one-dimensional system in Figure 5-4 and using equation (2.7), equation (5.9) can be written

$$\frac{\partial \rho_2}{\partial t} - v\frac{\partial \rho_2}{\partial x} = D\frac{\partial^2 \rho_2}{\partial x^2}, \tag{5.10}$$

Vilker *et al.* obtained an analytical solution to equation (5.10) using the boundary conditions

$$\rho_2 = \rho_2^0, \text{ all } x, \ t = 0, \tag{5.11}$$

$$\rho_2 = \rho_2^0, \ x = \infty, \text{ all } t, \tag{5.12}$$

and

$$\rho_2 v = -D\frac{\partial \rho_2}{\partial x}, \ x = 0, \text{ all } t, \tag{5.13}$$

where ρ_2^0 is the bulk solution concentration.[3] Vilker *et al.* also used the expression

$$v = L_p(\Delta p - \sigma \Delta \pi), \tag{5.14}$$

to describe the permeate flux as a function of time. In equation (5.14), L_p is the membrane resistance (assumed constant and equal to the resistance of pure solvent), Δp is the driving pressure, $\Delta\pi$ is the difference in the osmotic pressure across the membrane and σ, the reflection coefficient, is a measure of the ability of the membrane to reject solute ($\sigma = 1$ in Vilker *et al.*'s experiments).[4]

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[3] Equation (5.13) may be obtained from Fick's law, equation (5.7), using Figure 5-4, equation (2.11) and the boundary condition $v_2 = 0$ at $x = 0$.

Vilker *et al.* then used their solution to find an apparent value for D which gave the best fit to their concentration profile measurement. This can be viewed as a test of the assumption that pressure gradients were negligible in Vilker *et al.*'s system. Equations (5.10) to (5.14) have traditionally been used to study reverse osmosis systems, where the assumption of uniform pressure appears to have been valid. If these equations apply within Vilker *et al.*'s system, then we would expect their prediction of the diffusion coefficient to correspond with experimental measurements from the literature. Vilker *et al.*'s analysis predicts a diffusion coefficient of $D = 30\times10^{-7} cm^2/s$. Their experimental conditions (experiment K) were $0.15M$ NaCl as the solvent, pH 7.4, 25^0 C. Experimental measurements of D, using ultracentrifuge and light-scattering experiments, under conditions similar to those of Vilker *et al.*, predict a diffusion coefficient of between $5\times10^{-7} cm^2/s$ and $10\times10^{-7} cm^2/s$ over the concentration range used by Vilker *et al.* (see Figures 5-3 and 5-5). The discrepancy between the diffusion coefficient predicted by Vilker *et al.* and the measurements from ultracentrifuge and light-scattering experiments is quite significant. Vilker *et al.* [1981, p644] suggested that the discrepancy may have been due to "uncertainties as to the true value" of D and due to "diffusion potential effects". What portion of the discrepancy can be explained by these effects is still open to question. Another possible explanation is that pressure gradients existed within Vilker's system, and that a more general system of equations, such as (3.17) through (3.21), should be used to describe flow within the concentration polarization layer rather than the convective-diffusion equation.

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[4] Equation (5.14) appears to be a result obtained from the nonequilibrium thermodynamics of membrane transport. To our knowledge, equations of this type have only been rigorously derived for systems in which the solution properties on either side of the membrane are uniform. Thus, Δp and $\Delta\pi$ are considered to be the difference in pressure and osmotic pressure between the bulk solution on either side of the membrane. For a review of such theorems, see Baranowski [1991] or Mason and Lonsdale [1990]. In order to account for the presence of a concentration polarization layer, these theorems should be generalized to allow for varying properties on either side of the membrane. We will not attempt such a development here; however, we note that the final results are likely identical except that Δp and $\Delta\pi$ would refer to differences in conditions between the membrane surfaces rather than between the bulk solutions. Vilker *et al.* [1981] appear to have made such an assumption in their development.

Note that equation (5.14), when $\sigma = 1$, bears a resemblance to the modified Darcy's law, equation (3.14). These two equations should be distinguished from each other, as they were derived under different assumptions and apply to different physical phenomena. The modified Darcy's law is a local equation describing the solvent flux within a binary concentration polarization layer, whereas equation (5.14) is an integrated equation describing the permeate flux across a semipermeable membrane.

In 1996, Boulanouar, Nicolas and Bariou performed almost identical experiments to those of Vilker *et al.* (dead-end ultrafiltration of BSA in 0.15*M* NaCl, pH 7.4, 25^0 C, using an inert membrane with $\sigma = 1$), except that Boulanouar *et al.* only measured the permeate flux as a function of time; they did not measure the concentration profile. Boulanouar *et al.* used experimental data for the diffusion coefficient and attempted to predict their permeate flow measurements by solving the convective-diffusion equation numerically. Similarly to Vilker *et al.*, they found that their theoretical predictions did not match their experimental measurements. Boulanouar *et al.* attempted to explain the discrepancy by considering the osmotic pressure. They suggested that "in the case of charged solutes, the physicochemical properties of the solute (in particular, the osmotic pressure) are not directly useable when strong concentration gradients occur. . . . In the case of protein, the assumption of local variations in the environment of the BSA (H^+ concentrations, *etc.*) which may induce local modification of the osmotic pressure, can be reasonably advanced" [Boulanouar, 1996, p92]. Boulanouar *et al.* are assuming that the osmotic pressure and other physicochemical properties of charged solutes like BSA, obtained experimentally as functions of concentration under equilibrium conditions, are no longer the same functions of concentration under nonequilibrium conditions; essentially, they are claiming that the local equilibrium assumption is not valid within concentration polarization layers.

Certainly such an explanation for the discrepancy is possible. At present, there is no method to determine *a priori* the range of validity of the local equilibrium assumption, as discussed in Section 2.3.1; it is left for experiment to decide. However, we feel that the local equilibrium assumption should not be discarded until all other less drastic explanations for the discrepancy have been exhausted. One explanation that seems plausible is that pressure gradients were affecting flow within the concentration polarization layer. In fact, Bowen and Williams in 1996 obtained good predictive results for the permeate flux during dead-end ultrafiltration of BSA by assuming that flow within the layer was governed by Darcy's law. Bowen and Williams essentially used compressible cake filtration theory, which applies to concentration polarization layers in which the solute particles are large enough to neglect Brownian diffusion processes [Tiller, 1975]. Bowen and Williams' analysis is very interesting in that they developed a theoretical model of particle-particle interactions allowing them to predict the osmotic pressure and diffusion coefficient of BSA as functions of concentration [Bowen, 1996a; Bowen, 1998]. However, the problem with their analysis is that, after developing a very accurate model for the osmotic pressure and diffusion coefficient of concentrated macromolecular or colloidal solutions, they failed to take diffusion into account in their flow equations.

To summarize, Vilker *et al.* [1981] and Boulanouar *et al.* [1996] neglected pressure gradients in their analysis of BSA filtration, similarly to reverse osmosis theorists. Bowen and Williams [1996b] attacked the problem from a different point of view and neglected diffusion processes, similarly to compressible cake filtration theorists. It seems that Bowen and Williams' assumption may have been more valid, as their theoretical analysis gave good predictions of their experimental measurements, at least for certain pHs and ionic conditions. However, for some range of particle sizes, pHs and ionic conditions, it will no longer be valid to neglect diffusion processes or pressure gradients; both effects will have to be accounted for simultaneously. A more general system of equations, such as (3.17) through (3.21), should be used to predict the temporal behaviour of such systems.

5.2.3 ***Kim* et al.*'s [1991] Permeability Prediction***

In 1991, Kim *et al.* attempted to use Vilker *et al.*'s [1981] data to obtain a measurement of the permeability of BSA. They assumed that the modified Darcy's law, equation (3.14), could be used to describe flow within Vilker *et al.*'s system:

$$\boldsymbol{v}_{Da} = -\frac{k}{\eta_1}(\nabla p - \nabla_T\pi). \tag{5.15}$$

As we saw in Section 3.2, the modified Darcy's law is valid only if the solute velocity $\boldsymbol{v}_2$ is zero. If there had been a fixed amount of BSA placed above the membrane in Vilker *et al.*'s experiments, with the rest of the bulk solution being pure solvent, as in Gowman's experiments [Gowman, 1996], we would expect that over time the solute would rearrange itself against the membrane and its velocity would become zero, allowing the modified Darcy's law to be used. However, in Vilker *et al.*'s system, the bulk solution contained $0.1g/cm^3$ BSA; therefore, the solute continually built up against the membrane and $\boldsymbol{v}_2$ never became zero. Certainly very near the membrane we would expect the solute velocity to be near zero, since the membrane was almost 100% rejecting to BSA; however, farther up the concentration polarization layer, where the solute concentration approaches the bulk solution concentration, the solute velocity approaches the bulk velocity and the assumption of zero solute velocity is not valid. The equation Kim *et al.* should have used when attempting to model Vilker *et al.*'s system is equation (3.13):

$$\boldsymbol{J}_1 = -\left(\frac{c_2}{\upsilon_1}\right)\frac{k}{\eta_1}(\nabla p - \nabla_T\pi). \tag{5.16}$$

It was assumed by Kim *et al.* that pressure gradients within Vilker's system were zero or negligible. Thus, they reduced equation (5.15) to

$$\boldsymbol{v}_{Da} = \frac{k}{\eta_1}\nabla_T\pi. \tag{5.17}$$

Vilker *et al.* measured the velocity $\boldsymbol{v}_f$ of the filtrate leaving the system; this value was used by Kim *et al.* as an approximation to $\boldsymbol{v}_{Da}$. Thus, equation (5.17) can be written, for the one-dimensional system shown in Figure 5-4,

$$v_f = -\frac{k}{\eta_1}\left(\frac{d\pi}{dx}\right)_T = -\frac{k}{\eta_1}\left(\frac{\partial\pi}{\partial\rho_2}\right)_T\frac{d\rho_2}{dx}. \tag{5.18}$$

Also, Vilker *et al.* measured the osmotic pressure π as a function of BSA concentration and they measured the solute concentration as a function of distance from the membrane [Vilker, 1981]. Using the viscosity of pure water for η_1, all of the factors in equation (5.18) are known except for k.

Figure 5-6 shows the prediction of k made using equation (5.18), along with a fit of experimental data for k obtained by Kim *et al.* from sedimentation studies [Kim, 1991, equation (13), p409]:

$$k = 1.6\times10^{14}\rho_2^{-1}(1 - 1.348\rho_2)^{5.1}. \tag{5.19}$$

As expected, the prediction of k using equation (5.18) gets worse as the solute concentration approaches $0.1 g/cm^3$, and the assumption $v_2 = 0$ becomes less valid. In their paper, Kim *et al.* [1991, p407] note that the predictions of k made using equation (5.18) "appear to deviate from the general behavior for concentrations ~ $0.1 g/ml$." In fact, the value of k predicted using equation (5.18) asymptotically approaches infinity as the concentration approaches $0.1 g/cm^3$. The reason for this is that $\frac{d\rho_2}{dx}$ approaches zero as ρ_2 approaches $0.1 g/cm^3$. All of the other factors in equation (5.18), v_f, η_1 and $\left(\frac{\partial\pi}{\partial\rho_2}\right)_T$, remain finite and non-zero; therefore, equation (5.18) predicts that k will go to infinity as ρ_2 approaches the bulk concentration.

5.2.4 *Kim* et al.*'s [1991] Pressure Measurements*

Before concluding our study of BSA, we note that Kim *et al.* [1991] obtained direct measurements of the pressure profile within an ultrafiltration system using BSA as the solute (buffered saline of unspecified ionic strength as the solvent, pH 7.3). They placed a fixed amount of BSA solution above the membrane, on top of which was placed a bulk solution containing pure solvent. Their experiments were run for a month, to allow "the concentration polarization layer to reach an equilibrium state" [Kim, 1991, p406]. Their pressure measurements are reproduced on Figure 5-7. Studying the profile, there appears to be some deviation in the pressure near the membrane; however, these changes are insignificant compared to the overall driving pressure. The purpose of Kim *et al.*'s pressure measurements was to verify the theoretical predictions of Wales [1981], Wijmans *et al.* [1985] and Johnson *et al.* [1987] that pressure gradients are zero in macromolecular concentration polarization layers. However, as we saw in Chapter 4, these theories are not valid. Thus, there are no theoretical reasons for assuming that pressure gradients were zero in Kim *et al.*'s system.

The measurements of Kim *et al.* provide evidence that any pressure drop across the layer was negligible compared to the overall driving pressure; however, the measurements do not provide evidence that pressure gradients were zero. Had Kim *et al.* used a membrane that was highly resistant to adsorption, for example a cellulose-acetate membrane, so that none of the pressure drop occurred across an adsorption layer or due to an increased resistance of the membrane caused by fouling and pore occlusion, then their experimental results would give strong evidence that the layer behaves more like a region undergoing ordinary diffusion than like a porous medium or compressible filter cake. However, Kim *et al.* used a PTGC 02510 membrane (Millipore, Bedford, MA) [Kim, 1991, p407]; these membranes are polysulfone and have "a relatively high non-specific binding capacity compared to other membranes such as regenerated cellulose" [Leary, 1999]. It is known that polysulfone membranes tend to adsorb large quantities of BSA during ultrafiltration [Nabe, 1997; Fernandez-Torres, 1998]. If BSA molecules were adsorbing to the surface and within the pores of the membrane used by Kim *et al.*, then it is possible that most of the pressure drop occurred across the adsorption layer and membrane, making it difficult to use their measurements to indicate whether the concentration polarization layer was behaving as a region undergoing Brownian diffusion, as a porous medium, or as some combination.

5.3 *Hyaluronate (HA)*

In this section, we will review the experimental results from the ultrafiltration of the biopolymer hyaluronate (HA) obtained by Gowman [1996], as they provide evidence that pressure gradients were affecting flow within the system. We will also attempt to predict the pressure profile in Gowman's system. Finally, we will discuss the HA permeability measurements of Jackson and James [1982], as they provide an example of the different viewpoints used to explain the concentration polarization phenomenon.

5.3.1 *HA Ultrafiltration*

In 1996, Gowman made concentration profile measurements within the polarization layer of a dead-end ultrafiltration system containing the biopolymer sodium hyaluronate (HA) dissolved in $0.01M$ NaCl. In those experiments, a fixed amount of solution was placed above the membrane; the bulk solution above the HA contained pure solvent (see Figure 5-8). A constant flowrate was maintained within the system until the solute rearranged itself against the membrane and became stationary (approximately 40 hours). Concentration profile measurements were taken every few hours. The experimental data obtained by Gowman is very amenable to analysis because the system reached a steady-state in which the solute was stationary. Therefore, the modified Darcy's law, or an equivalent expression, may be used directly to predict the steady state pressure profile.[5]

On page 124 of Gowman's thesis, it was concluded that pressure gradients may have existed within the concentration polarization layer. There were both theoretical and experimental reasons for coming to such a conclusion. First, Gowman reviewed two theories of concentration polarization [Wijmans, 1985; Johnson, 1987] purporting to show that pressure gradients are zero within concentration polarization layers. Wijmans *et al.* [1985] assumed that the layer was Newtonian, a condition which Gowman believed was likely violated in her experiments.[6] Also, Gowman attempted to analyse her data while working under the assumption of zero pressure gradients, and the results did not always appear to support such a conclusion. We will review the data analysis given in Gowman's thesis next and then make an attempt at predicting the pressure profile within her system.

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[5] Note that considerable adsorption of HA on the membrane surface and within the pores likely occurred in Gowman's experiments [Gowman, 1996, p114-117]. As our model is incapable of describing adsorption phenomena, we will assume that the adsorption had no other effect on the concentration polarization layer than to make it behave as though it were above an inert membrane with a higher resistance to flow (*i.e.* we are assuming that the adsorption layer above the membrane increased the resistance of the membrane but did not interact with, or have any other effect on, the concentration polarization layer).

Gowman [1996, p25] assumed that the modified Darcy's law, equation (3.14), could be used to describe her steady-state data:

$$\mathbf{v}_{Da} = -\frac{k}{\eta_1}(\nabla p - \nabla_T \pi). \tag{5.20}$$

Neglecting pressure gradients, noting that Gowman's system was one dimensional (see Figure 5-8) and assuming that the solvent volume velocity $\mathbf{v}_{Da}$ is given by

$$\mathbf{v}_{Da} = \frac{Q}{A}(-\hat{i}), \tag{5.21}$$

where Q is the volumetric flowrate and A is the flowcell cross sectional area, equation (5.20) may be written

$$\frac{Q}{A} = -\frac{k}{\eta_1}\left(\frac{d\pi}{dx}\right)_T = -\frac{k}{\eta_1}\left(\frac{\partial \pi}{\partial c_2}\right)_T \frac{dc_2}{dx}. \tag{5.22}$$

Gowman integrated equation (5.22) (equation (34) of her thesis), using $c_2(x = l_f) = 0$ as a boundary condition, where l_f is the final layer thickness, in order to predict her experimental concentration profiles. She used experimental data for k and π from the literature. The result is reproduced on Figure 5-9. The concentration profile predicted using equation (5.22) does not match the experimental data very well. One possible explanation for the discrepancy is uncertainty as to the true values of k and π, due to scatter in the literature data and due to varying conditions (ionic strength, pH, molar mass) between Gowman's ultrafiltration experiments and the experiments performed to measure k and π. The permeability values used by Gowman were actually obtained from measurements of the sedimentation coefficient $\tilde{s}$ [Ethier, 1986]. The sedimentation measurements were performed using $0.2M$ NaCl as the solvent, ionic conditions far removed from the $0.01M$ NaCl solvent used by Gowman. Also, the pHs and HA molar masses used in the sedimentation experiments varied somewhat from Gowman's experiments. We were unable to find any reliable sedimentation coefficient or permeability measurements performed under the same ionic conditions used by Gowman; therefore, we do not know what effect such data would have on the concentration profiles predicted using equation (5.22). Also, Gowman used the osmotic pressure measurements of Peitzsch and Reed [1992], obtained using $0.01M$ NaCl as the solvent. Their data was quite scattered and biased toward higher HA concentrations than those used by Gowman. Thus, it is possible that using accurate data for both π and k in equation (5.22) might yield a better prediction of Gowman's measured profile. Another possible explanation for the discrepancy is that pressure gradients were influencing the flow within Gowman's system and that equation (5.20) should have been used rather than (5.22). Before studying this possibility further, we will review Gowman's attempts to predict the diffusion coefficient D of HA using her experimental data, as this will yield further evidence for the existence of non-zero pressure gradients.

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[6] As we saw in Chapter 4, the theories that Gowman reviewed are not valid, even within Newtonian concentration polarization layers.

To predict the diffusion coefficient, Barry, Gowman and Ethier [1996] and Gowman [1996] employed essentially the same method used by Vilker *et al.* [1981] when predicting the diffusion coefficient of BSA.[7] They assumed that Fick's law described the diffusive flux within the system (therefore, they assumed no pressure gradients) and obtained the convective-diffusion equation (5.9):

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[7] See Section 5.2.2 for a summary of Vilker *et al.*'s analysis.

$$\rho\frac{\partial c_2}{\partial t} + \rho\boldsymbol{v}\cdot\nabla c_2 = \nabla\cdot\rho D\nabla c_2. \tag{5.23}$$

Due to the low solute concentrations used in Gowman's experiments, it was assumed that the density was constant [Gowman, 1996, p39]. Thus, equation (5.23) can be written

$$\frac{\partial c_2}{\partial t} + \boldsymbol{v}\cdot\nabla c_2 = \nabla\cdot D\nabla c_2. \tag{5.24}$$

Gowman's system was one-dimensional [Barry, 1996, p4] and it was assumed that the barycentric velocity could be approximated by

$$\boldsymbol{v} = U(-\hat{i}), \tag{5.25}$$

where U is the "superficial solvent velocity":

$$U = \frac{Q}{A}. \tag{5.26}$$

Thus equation (5.24) can be written

$$\frac{\partial c_2}{\partial t} = U\frac{dc_2}{dx} + \frac{d}{dx}\left(D\frac{dc_2}{dx}\right). \tag{5.27}$$

Equation (5.27) is equivalent to equation (1) of the paper by Barry *et al.* [1996] and was solved numerically to fit for the diffusion coefficient which gave the best approximation to Gowman's unsteady-state concentration profile measurements. This method required the use of an assumed functional form for D since the diffusion coefficient of HA is dependent on concentration. An alternative method, which required no assumed form for D, was to use the steady-state data obtained by Gowman. At steady-state ($\boldsymbol{v}_2 = 0, \frac{\partial c_2}{\partial t} = 0$), equation (5.27) can be integrated, using $c_2(x = \infty) = 0$ as a boundary condition, to yield

$$0 = Uc_2 + D\frac{dc_2}{dx}. \tag{5.28}$$

Equation (5.28) is Fick's law (equation (5.7) with $v_2 = 0$ and $v = -U\hat{i}$), and was used by Barry *et al.* to obtain a direct measurement of the diffusion coefficient (see Figure 5-10).

The data in Figure 5-10 is quite nonlinear, a result which was not expected by Barry *et al.* [1996, p5]; rather, it was thought that the diffusion coefficient would follow the form

$$D = ac_2^b, \tag{5.29}$$

where a and b are constant fitting parameters. Wik and Comper [1982] and Ghosh *et al.* [1990] measured D under similar ionic conditions to those of Gowman. Their data is plotted on Figure 5-10 as well; unfortunately, Ghosh *et al.*'s data yields only one data point measured at $0.001g/cm^3$ [Gowman, 1996, p18] and Wik and Comper made measurements up to only $0.006g/cm^3$. Since Barry *et al.*'s prediction extends up to $0.016g/cm^3$, we are unable to make a full comparison with experimental data from other sources. It was suggested by Barry *et al.* that the nonlinearities in Figure 5-10 are "transition points", and the lower transition point was thought to represent a transition of the solution from a semidilute to a homogeneous concentration regime [Barry, 1996, p8; Gowman, 1996, p118]. No explanation was offered for the other transition point. Another possible explanation is that pressure gradients were affecting flow within Gowman's system, and that the apparent nonlinear "transition points" in Figure 5-10 are not real, but are artifacts of using Fick's law to describe flow within the layer rather than the more general modified Darcy's law or equation (3.20); we will investigate this possibility next.

5.3.2 *HA Pressure Profile*

Barry *et al.* [1996] assumed that Fick's law applied within the concentration polarization layer:

$$J_2 = -\rho D \nabla c_2, \tag{5.30}$$

and hence neglected pressure gradients. Assuming significant pressure gradients existed within Gowman's system, equation (3.20) can be used to describe the flow. Let use rewrite equation (3.20) in terms of component 2 using equation (2.9):

$$J_2 = -\rho D \nabla c_2 + \frac{c_2}{\upsilon_1} \frac{k}{\eta_1} \nabla p. \tag{5.31}$$

Gowman [1996] measured the flowrate, the total pressure drop and the steady-state concentration profile. If we could obtain accurate measurements of D, k or $\tilde{s}$ as a function of HA concentration from the literature, equation (5.31), or an equivalent expression, could be used directly to predict the steady-state pressure profile. Unfortunately, reliable data, obtained under the same conditions as those in Gowman's experiments, does not seem to exist for any of these coefficients. As we saw in Figure 5-10, Wik and Comper [1982] measured D under similar ionic conditions to those of Gowman, but not over the full concentration range. Several experimentalists have measured $\tilde{s}$ over the same concentration range as Gowman, but under different ionic conditions [Preston, 1965; Laurent, 1961; Laurent, 1960]. Jackson and James [1982] measured k under similar ionic conditions and over a similar concentration range; however, their results are not considered to be reliable.[8] Thus, data for HA is simply too inadequate to allow for any accurate predictions. However, we will make some predictions using the data we have, as we would like to obtain at least an estimate of the magnitude of the pressure variations predicted by equation (5.31).

Since $v_2 = 0$ we may use the flux equation in the form of the modified Darcy's law, equation (3.14), rather than equation (3.20). Equation (3.14) may be written, for the one-dimensional system shown in Figure 5-8 and rearranging for the pressure gradient,

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[8] See Section 5.3.3.

$$\frac{dp}{dx} = \frac{\eta_1}{k} v_{Da} + \left(\frac{\partial \pi}{\partial \rho_2}\right)_T \frac{d\rho_2}{dx}. \tag{5.32}$$

To obtain a pressure profile, we can integrate equation (5.32) using the boundary condition $p(x = l_f) = p_0$, where p_0 is the driving pressure measured by Gowman, and l_f is the height of the boundary layer, also measured by Gowman. For the permeability, we will use a fit of sedimentation data given by Ethier [1986, equation (6), page 104]:

$$k = 2.92 \times 10^{-16} \rho_2^{-1.47}, \quad (cm^2), \tag{5.33}$$

For the osmotic pressure, we will use a fit of Peitzsch and Reed's [1992] measurements of π given by Gowman [1996, equation (11), page 10]:

$$\pi = 5.7 \times 10^4 \rho_2 + 3.34 \times 10^8 \rho_2^2, \quad \left(\frac{dyne}{cm^2}\right), \tag{5.34}$$

For υ_1 and ρ we will use the values of pure water:

$$\upsilon_1 = \rho^{-1} = 1 cm^3/g. \tag{5.35}$$

For υ_2, we will assume a constant value of $0.6 cm^3/g$ [Gowman, 1996, p11]. Along with Gowman's measurements of v_{Da} and ρ_2, we have enough information to predict the pressure profile.

Note that the sedimentation coefficient measurements of the experiments analysed by Ethier [1986] were made using $0.2M$ NaCl as the solvent, an ionic regime far removed from the $0.01M$ NaCl used by Gowman. Unless the sedimentation coefficient is approximately independent of ionic strength over that range we cannot expect equation (5.32) to yield a very accurate prediction of the pressure profile. Also, Peitzsch and Reed's [1992] osmotic pressure measurements, although obtained under similar ionic conditions, were biased toward a higher concentration range than that of Gowman's experiments [Gowman, 1996, p10]. Figure 5-11 shows the pressure profile predicted using equation (5.32). It is conceivable that such a profile existed in the concentration polarization layer. It is a physically possible profile, at least.

The only reliable measurements of an empirical coefficient obtained under the same ionic conditions as used in Gowman's experiments that we were able to obtain are Wik and Comper's [1982] measurements of the diffusion coefficient. We may use equation (5.4), along with entries (4) and (5) of Table 2-1 and equations (2.109), (5.35), (2.14) and (2.7), to write equation (5.32) in terms of the diffusion coefficient. This yields, for the one-dimensional system shown in Figure 5-8,

$$\frac{dp}{dx} = \frac{\rho_2}{D}\left(\frac{\partial\pi}{\partial\rho_2}\right)_T v_{Da} + \left(\frac{\partial\pi}{\partial\rho_2}\right)_T \frac{d\rho_2}{dx}. \tag{5.36}$$

Wik and Comper measured the diffusion coefficient only up to a concentration of about $0.006 g/cm^3$, as shown on Figure 5-10, whereas Gowman's data extends up to about $0.016 g/cm^3$. It is not unreasonable to expect that the diffusion coefficient should be roughly linear over the concentration range of Gowman's experiment; therefore, we will linearly extrapolate Wik and Comper's data to a concentration of $0.016 g/cm^3$ using a fit of their data obtained by Gowman [1996, equation (24), page 17]:

$$D = 3.3\times10^{-4}\rho_2, \quad \left(\frac{cm^2}{s}\right). \tag{5.37}$$

Certainly we cannot be sure that such an extrapolation is valid; however, we will do the extrapolation anyway and see what equation (5.36) predicts. We will use Peitzsch and Reed's [1992] measurements of the osmotic pressure, which were obtained under the same ionic conditions as in Gowman's experiments ($0.01 M$ NaCl). Figure 5-12 shows the pressure profile predicted using equation (5.36). It is also a physically possible profile.

Given that equation (5.31) is a combination of Fick's law and Darcy's law, it would be interesting to predict the pressure profile using this equation as well; a benefit of using equation (5.31) is that we do not require any osmotic pressure data. At steady-state in Gowman's system, $\boldsymbol{v}_2$ is zero, and the diffusive flux $\boldsymbol{J}_2$ may be written, using equations (2.11), (2.6), (2.9) and (3.15),

$$J_2 = -\frac{c_2}{\upsilon_1} v_{Da} . \tag{5.38}$$

Inserting equation (5.38) into (5.31) and rearranging for the pressure gradient yields, using equations (2.9) and (5.35),

$$\frac{dp}{dx} = \frac{\eta_1}{k}\left(v_{Da} + \frac{D}{\rho_2}\frac{d\rho_2}{dx}\right). \tag{5.39}$$

Figure 5-13 shows the pressure profile predicted using equation (5.39). The profile has the same general shape as that predicted using equation (5.36). We did not have to use any π measurements in equation (5.39); however, we did have to use data for k that was obtained under $0.2M$ ionic conditions and we had to extrapolate to obtain data for D.

In Figure 5-14, we plotted the same profile as in Figure 5-12, but showing the entire pressure axis. The changes in pressure throughout the layer are predicted to be small compared to the overall driving pressure. This is in agreement with recent experimental measurements of the pressure profile within the HA layer of Gowman's system [Ethier, 1999]. Most of the pressure drop in Gowman's system was likely due to an increased resistance of the membrane caused by adsorption of HA on the surface of the membrane and within the pores, as discussed by Gowman [1996, pages 114-117]. Reducing the pressure drop caused by adsorption processes, for example by using an adsorption-resistant membrane, should yield a more pronounced pressure profile.

5.3.3 *Permeability Measurements of Jackson and James [1982]*

To conclude our discussion of HA ultrafiltration, we will look at the experiments of Jackson and James [1982], as they provide a further example of the different viewpoints that are used to explain the concentration polarization phenomenon in macromolecular systems. Both extremes of thought are represented. One group believed that diffusion processes were negligible and that the layer behaved as a porous medium, while another group suggested that pressure gradients were negligible and that only concentration gradients existed within the layer. In our review of the application of nonequilibrium thermodynamics to permeation in Section 2.6.2 we saw that, if one of the components of a binary solution could be held in place and at constant concentration by a *hypothetical* body force, then flow within the system could be modelled using Darcy's law. Jackson and James attempted to use Darcy's law to obtain a measure of the permeability of hyaluronate (HA) by measuring the total pressure drop across an HA matrix supported by a membrane.

Unfortunately, though the ideas presented in Section 2.6.2 are very useful from a theoretical point of view, in that they provide a relationship between the permeability and the sedimentation coefficient, they are impractical from an experimental point of view, in that it would be exceedingly difficult to apply a body force necessary to eliminate concentration gradients in an ultrafiltration experiment. In the experiments of Jackson and James, no attempts were made to apply such a force; rather, it was assumed that any concentration polarization of the HA against the membrane would not affect the permeability measurements. As pointed out by Parker and Winlove [1984], it is very likely that significant polarization occurred within the experiments of Jackson and James; even at very low flowrates of solvent through a HA solution, Parker and Winlove observed considerable concentration polarization against the membrane. Also, the permeability measurements of Jackson and James do not agree with permeability estimates from sedimentation studies [Ethier, 1986].[9]

Johnson, Kamm, Ethier and Pedley [1987], in agreement with Parker and Winlove [1984], suggested that the concentration gradients in the experiments of Jackson and James [1982] were not negligible. Instead, they claimed that the *pressure gradients* were negligible. They asserted that the discrepancy between the permeability measurements of Jackson and James and those obtained from sedimentation studies could be explained by using the modified Darcy's law without the pressure gradient term (essentially Fick's law) to model the flow. Johnson *et al.* claimed that the pressure drop measurements of Jackson and James were due to an osmotic pressure difference across the membrane caused by the increased concentration. However, as we saw in Section 4.2.5, Johnson *et al.*'s theoretical arguments for neglecting pressure gradients are not correct; thus, there is no theoretical reason to assume that the pressure drop across the HA layer of Jackson and James' experiments was zero. It seems likely that the pressure measurements and permeability measurements of Jackson and James [1982] were the result of the combination of three effects: a pressure drop across the HA layer itself, a pressure drop due to an osmotic pressure difference across the membrane, and an increased pressure drop across the membrane due to adsorption, pore occlusion and other solute-membrane interactions.

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[9] This discrepancy could be due in part to the fact that the ionic conditions used in Jackson and James' experiments (0.01M phosphate buffer) were in a regime far removed from the ionic conditions used in the sedimentation studies (0.2M to 0.3M phosphate buffered saline).

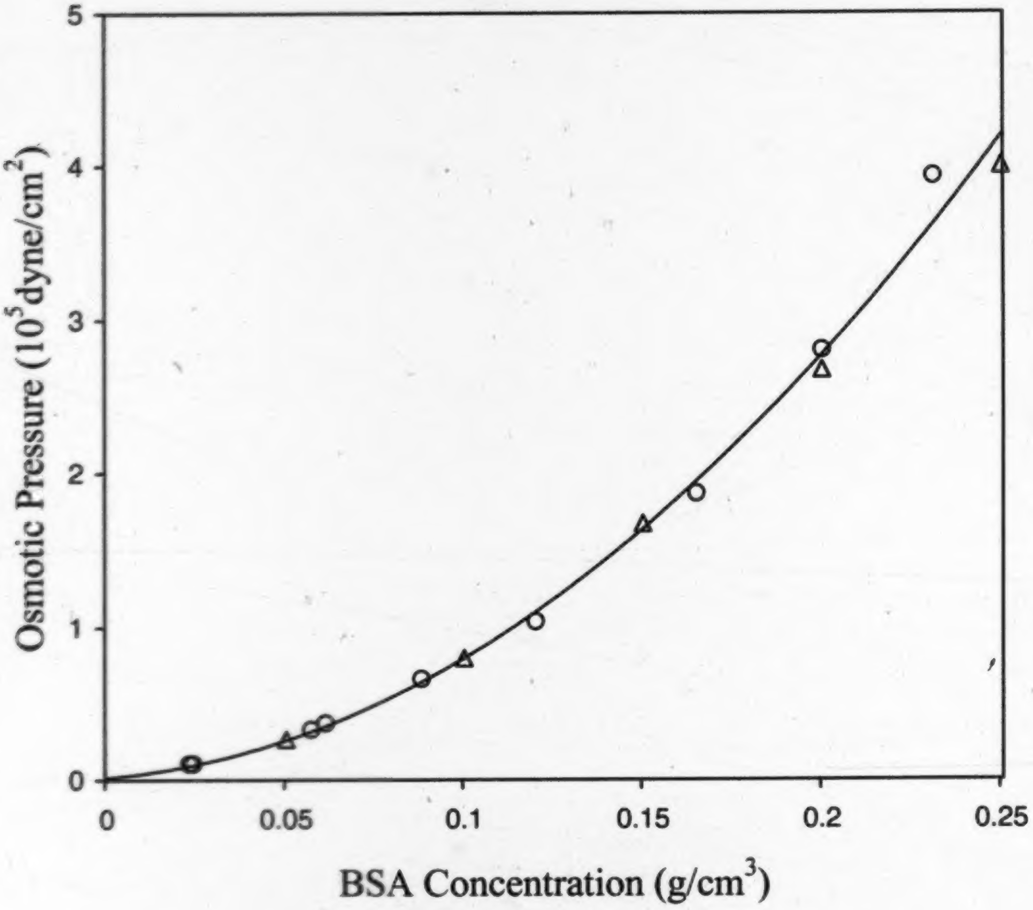

Figure 5-1: Osmotic pressure of bovine serum albumin (BSA). Measurements are from Scatchard *et al.* [1944], (o) and Kim *et al.* [1991] (Δ). The solid line is a fit of the data using a second order polynomial.

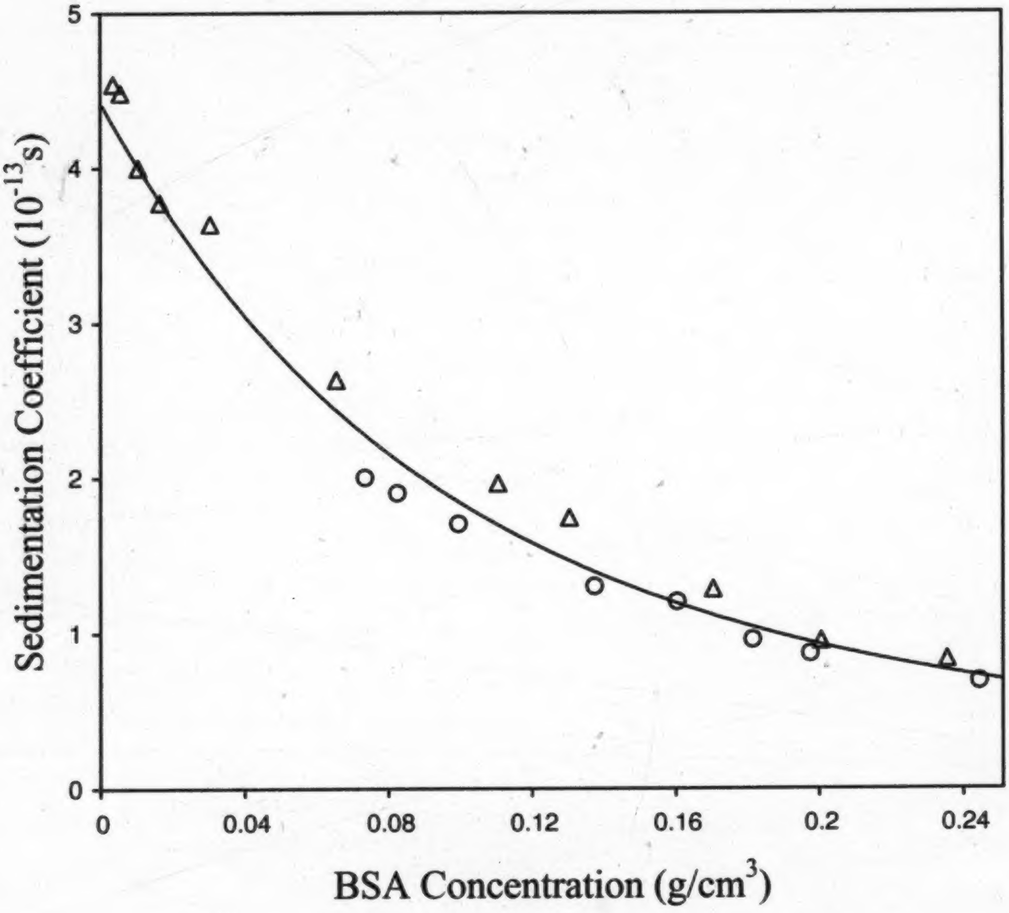

Figure 5-2: Sedimentation coefficient of bovine serum albumin (BSA). Measurements are from Comper and Zamparo [1989], (o) and van den Berg and Smolders [1989], (Δ). The solid line is a fit of the data using a second order polynomial.

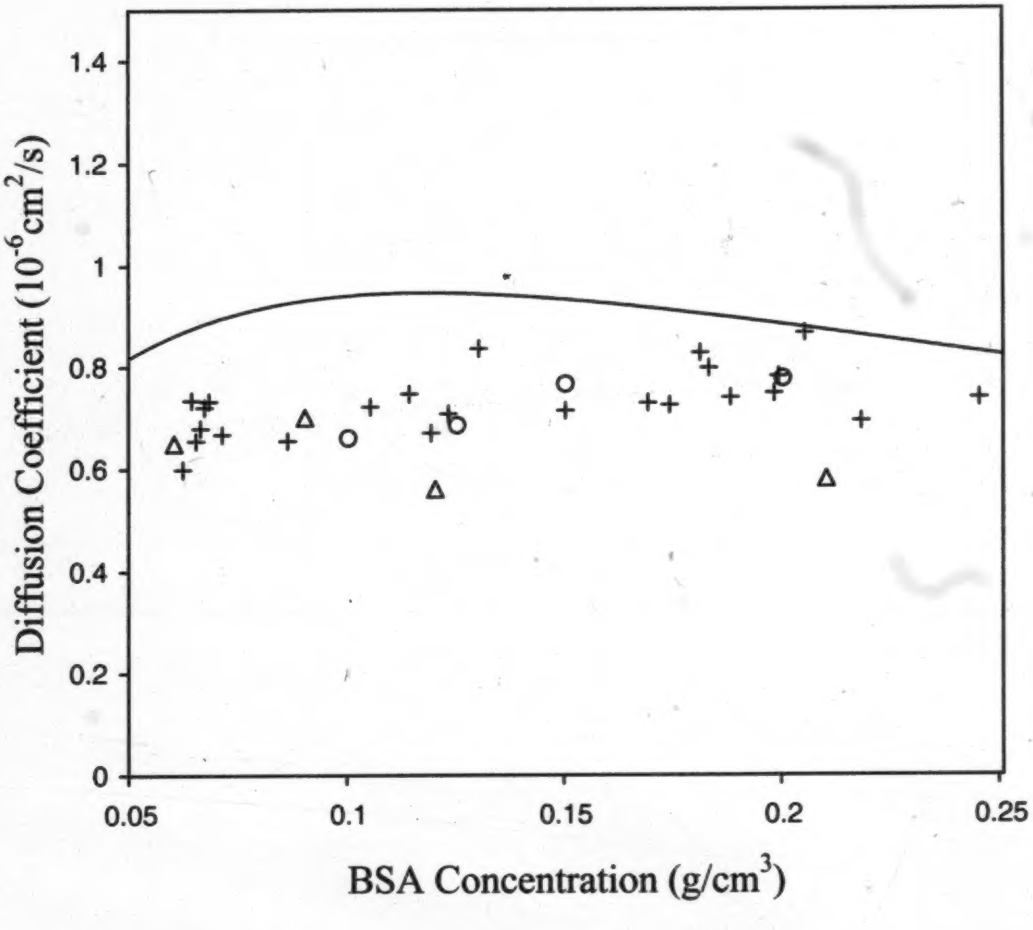

Figure 5-3: Diffusion coefficient of bovine serum albumin (BSA). Measurements are from Fair *et al.* [1978], (o), van den Berg and Smolders [1989], (Δ) and Phillies *et al.* [1976], (+). The solid line is the diffusion coefficient predicted using equation (5.4).

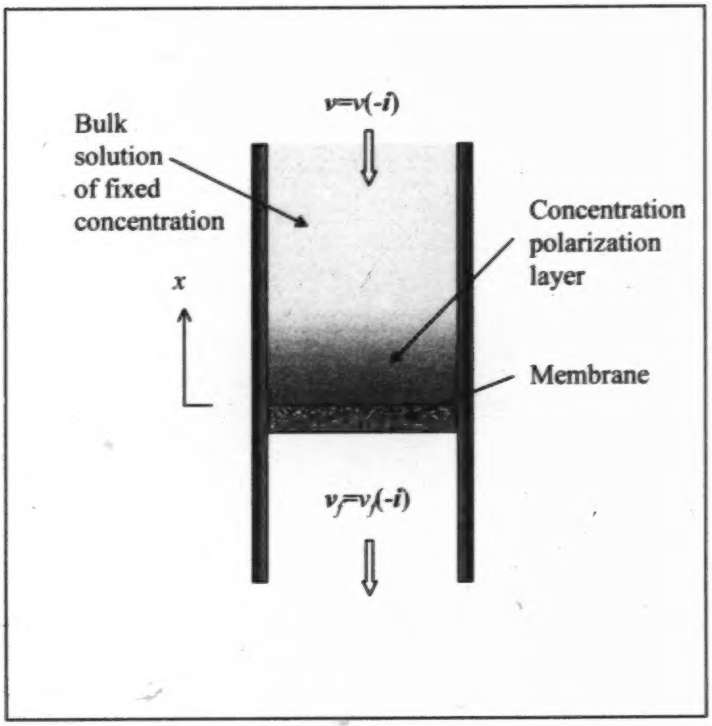
Bulk solution of fixed concentration
$\mathbf{v}=v(-\mathbf{i})$
x
Concentration polarization layer
Membrane
$\mathbf{v}_f=v_f(-\mathbf{i})$

Figure 5-4: Schematic of the ultrafiltration system used by Vilker *et al.* [1981]. The quantity $\mathbf{v}$ is the barycentric velocity and $\mathbf{v}_f$ is the filtrate velocity. The bulk solution contains a fixed concentration of solute.

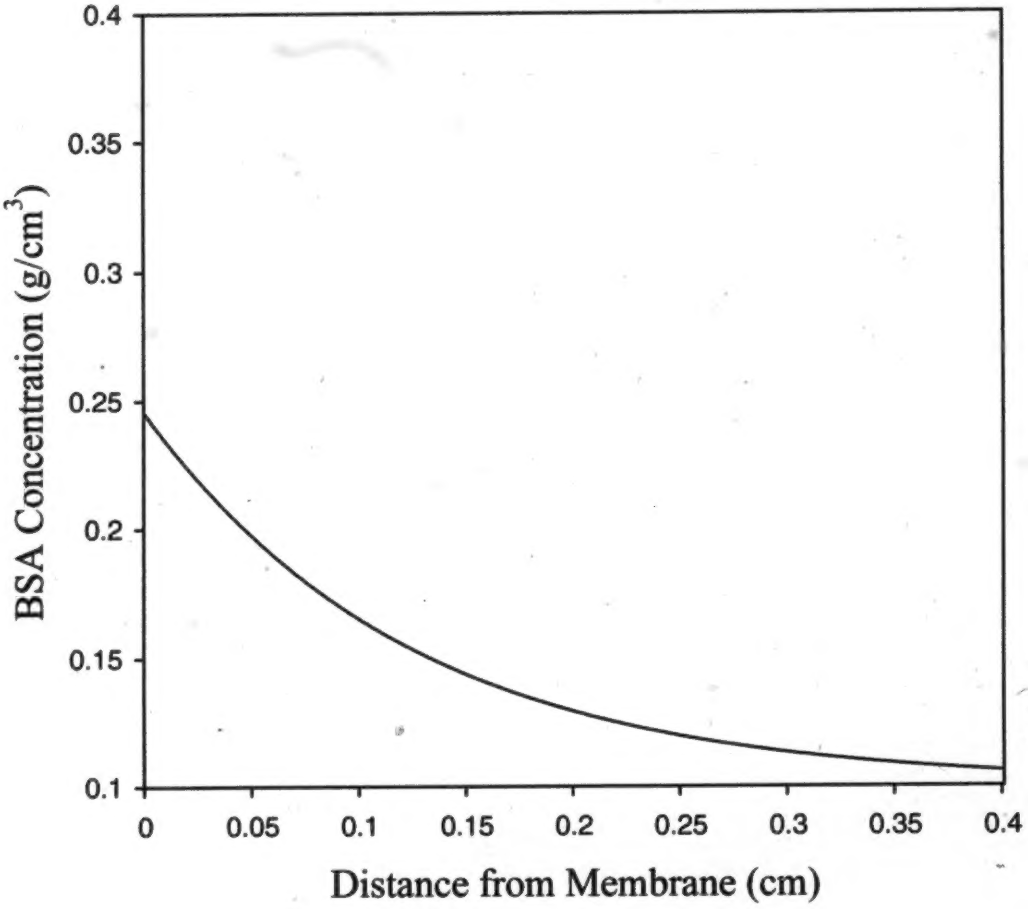

Figure 5-5: Concentration profile of bovine serum albumin (BSA) measured by Vilker *et al.* [1981] in their experiment K after approximately 9 hours.

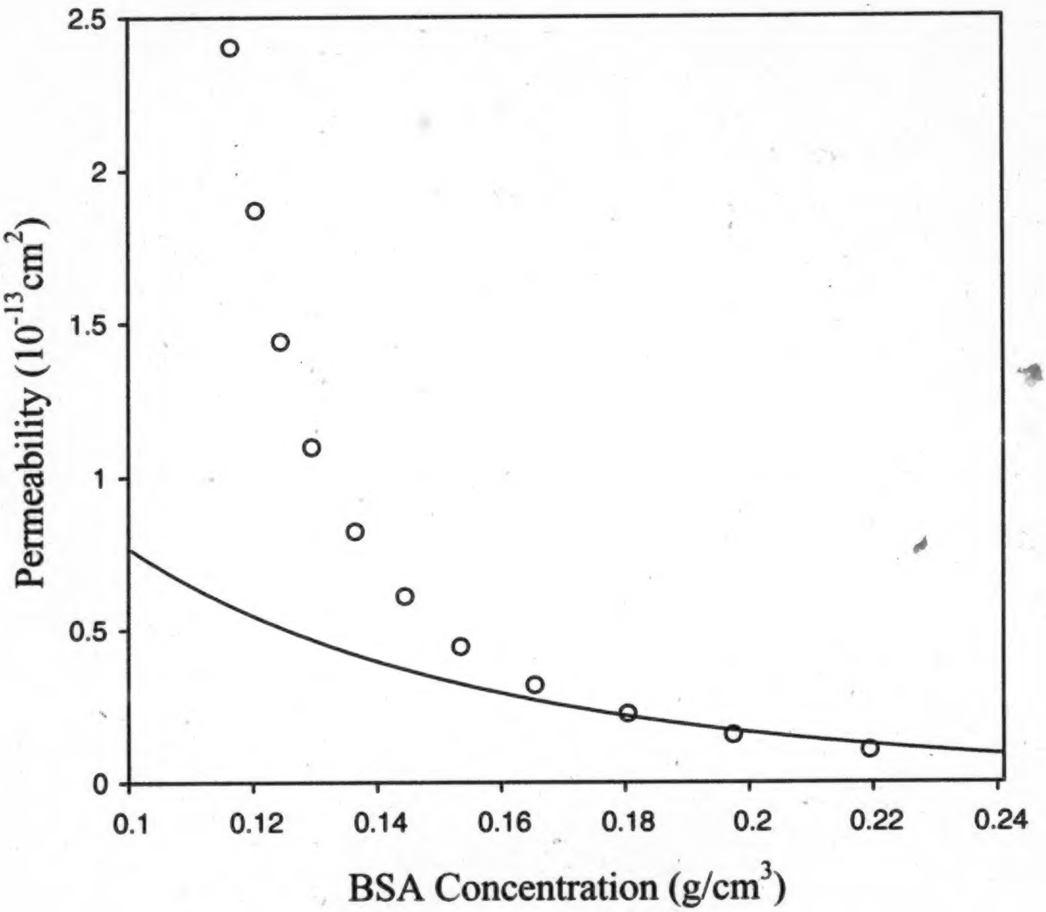

Figure 5-6: Permeability of bovine serum albumin (BSA). The solid line is a fit of sedimentation data and the open circles are the predictions of Kim *et al.* [1991].

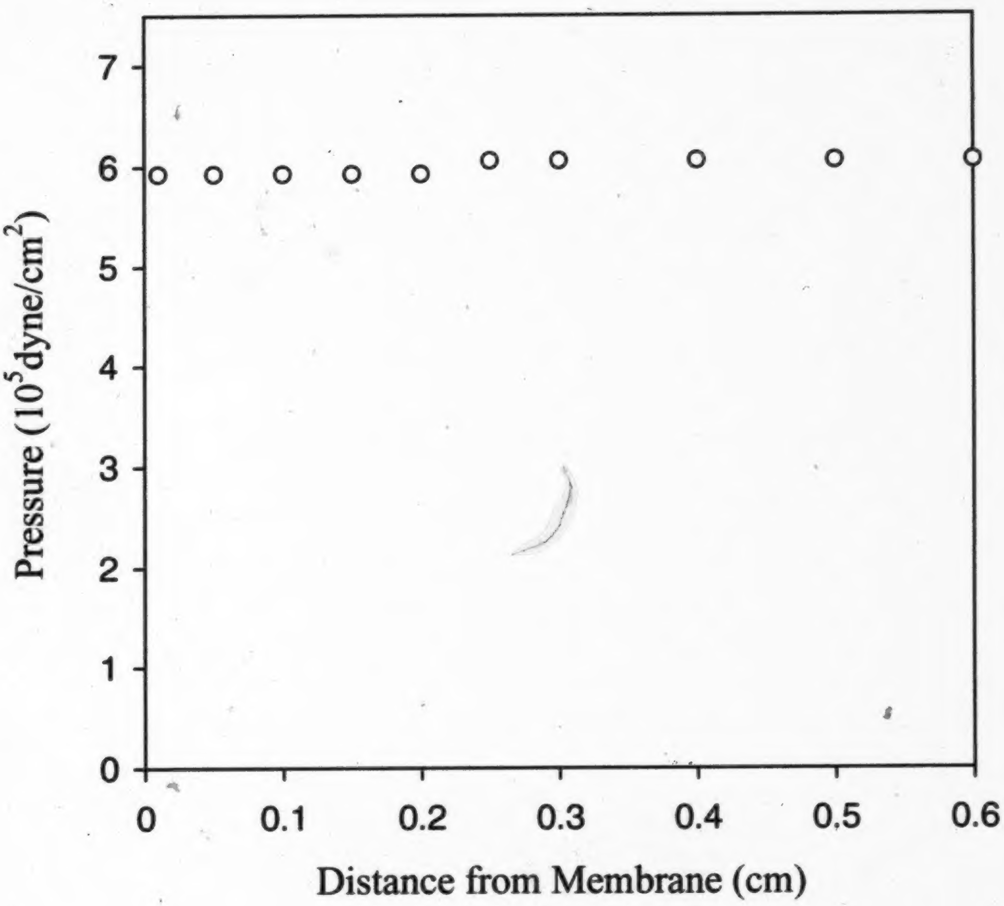

Figure 5-7: Pressure profile within an ultrafiltration system containing bovine serum albumin (BSA) measured by Kim *et al.* [1991].

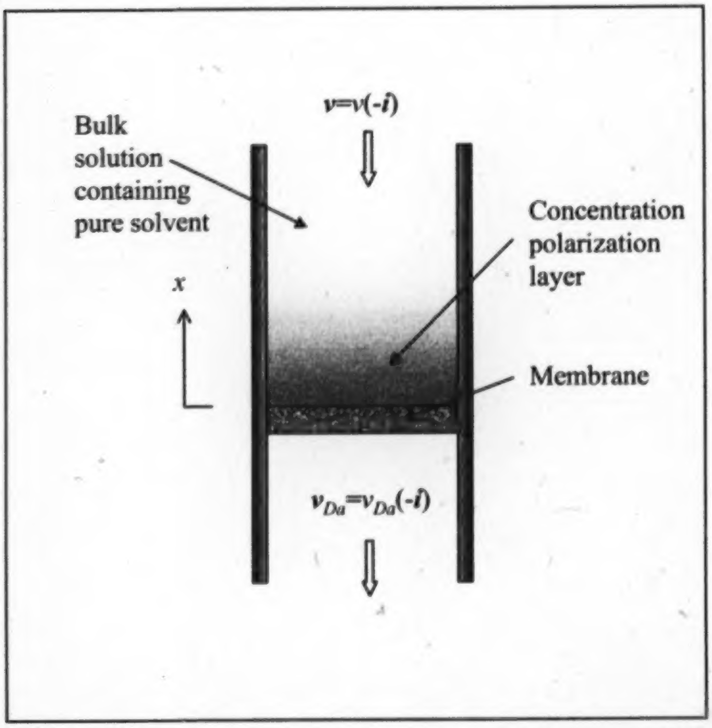
$\boldsymbol{v}=v(-\hat{\boldsymbol{i}})$
Bulk solution containing pure solvent
Concentration polarization layer
x
Membrane
$\boldsymbol{v}_{Da}=v_{Da}(-\hat{\boldsymbol{i}})$

Figure 5-8: Schematic of the ultrafiltration system used by Gowman [1996]. The quantity $\boldsymbol{v}$ is the barycentric velocity and $\boldsymbol{v}_{Da}$ is the velocity of the filtrate. The bulk solution contains pure solvent, in contrast to Vilker *et al.*'s [1981] system, which contained a fixed concentration of solute (see Figure 5-4).

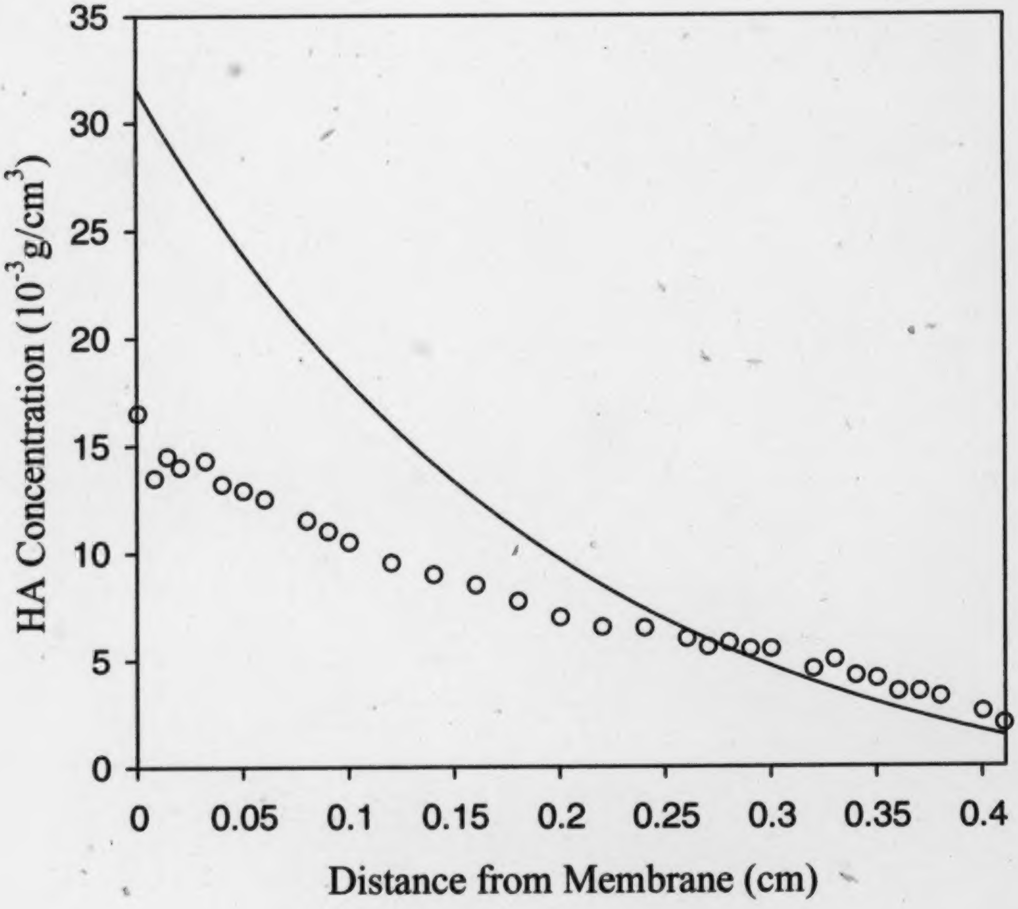

Figure 5-9: Steady-state concentration profile within an ultrafiltration system containing hyaluronate (HA). The open symbols are the measurements of Gowman [1996] and the solid line is a prediction assuming uniform pressure.

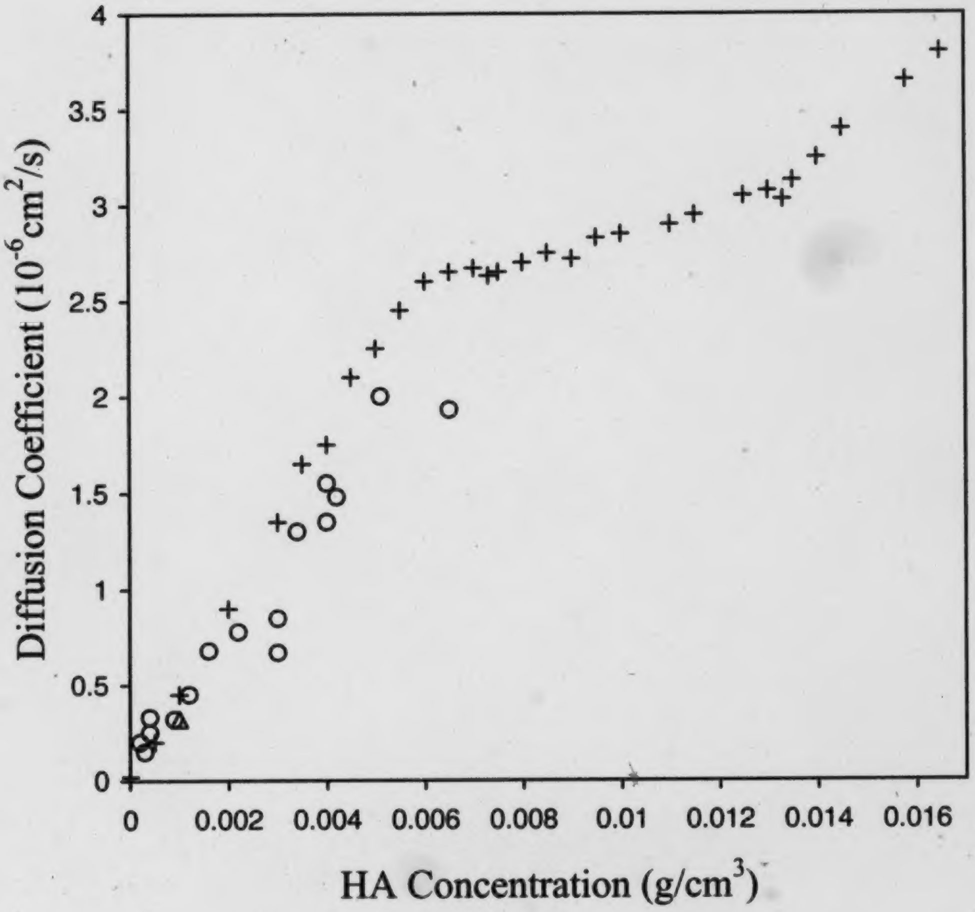

Figure 5-10: Diffusion coefficient of hyaluronate (HA) predicted by Barry *et al.* [1996], (+). Also shown are the diffusion coefficient measurements of Wik and Comper [1982], (o), and Ghosh *et al.* [1990], (Δ).

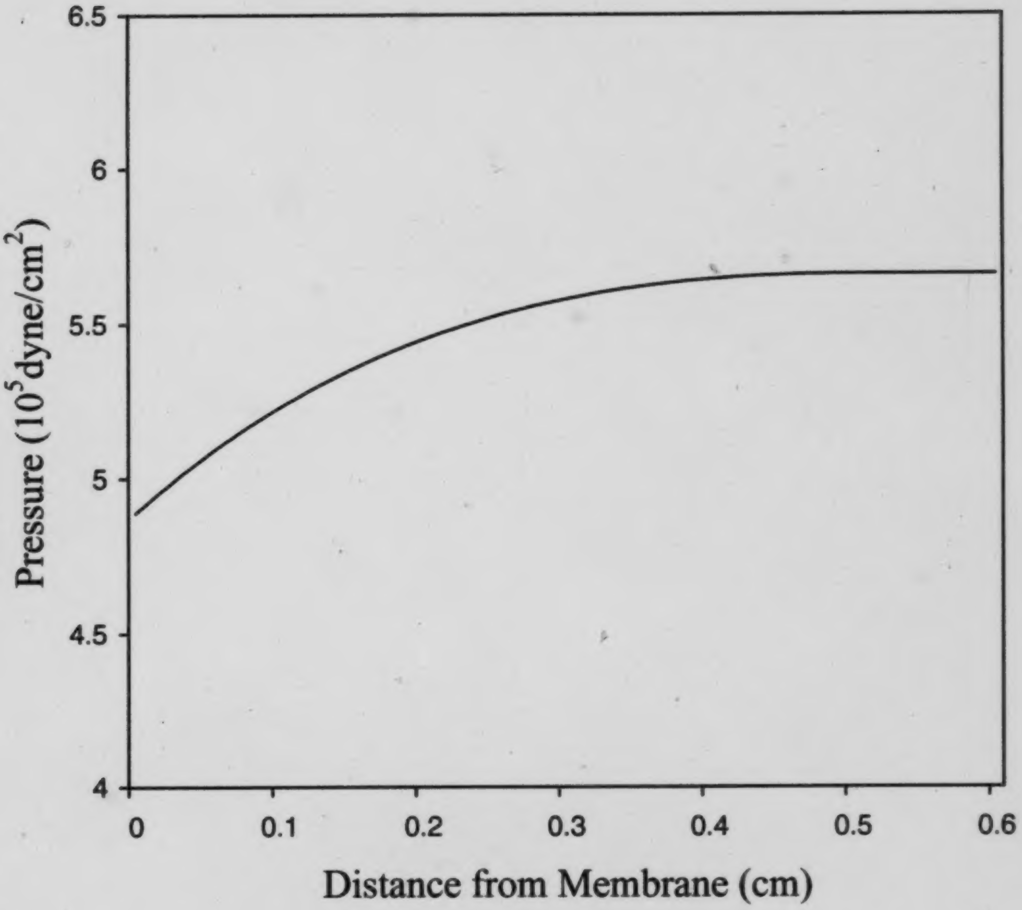

Figure 5-11: Steady-state pressure profile in Gowman's ultrafiltration system [1996], predicted using equation (5.32).

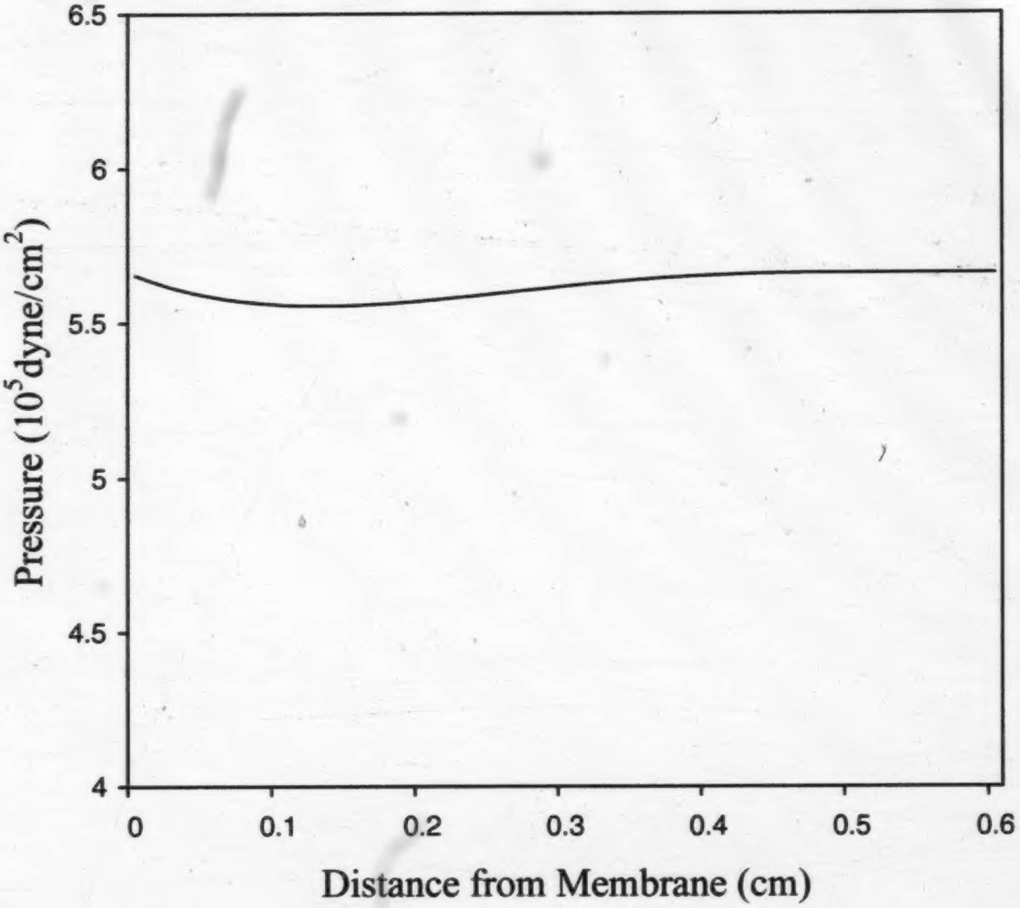

Figure 5-12: Steady-state pressure profile in Gowman's ultrafiltration system [1996], predicted using equation (5.36).

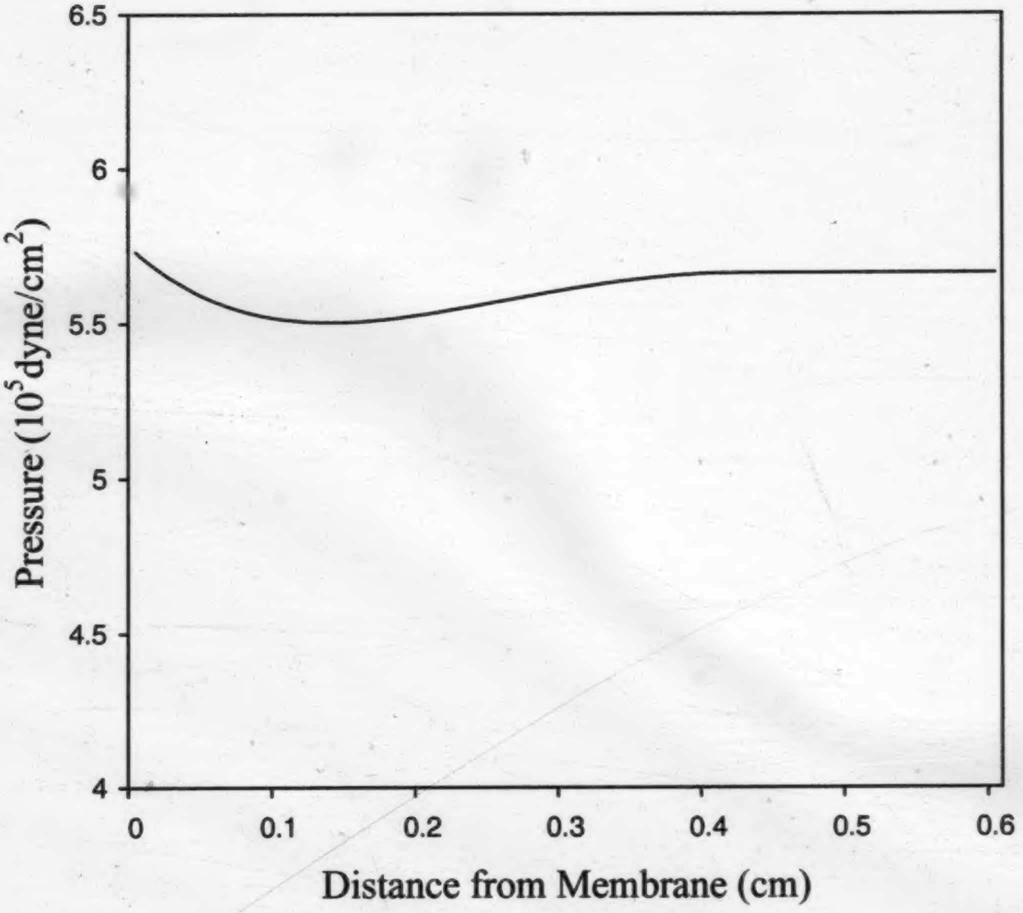

Figure 5-13: Steady-state pressure profile in Gowman's ultrafiltration system [1996] predicted using equation (5.39).

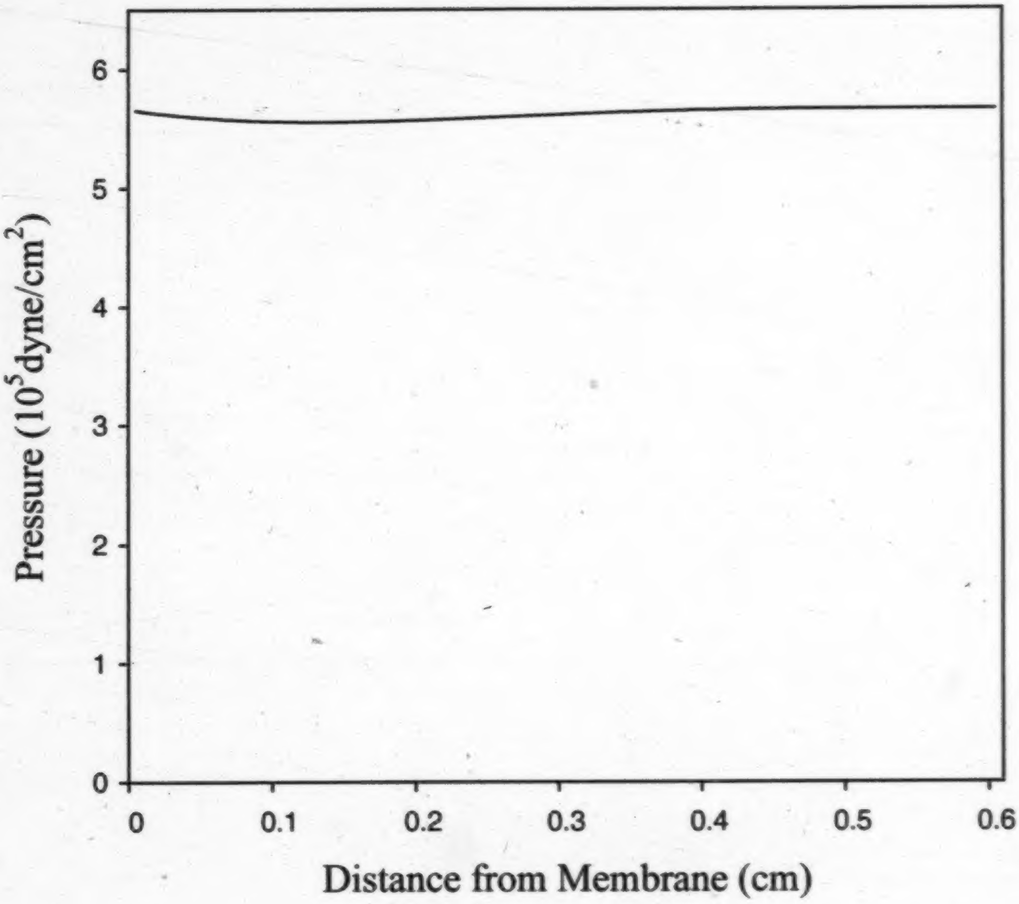

Figure 5-14: Same plot as in Figure 12, but showing the full pressure axis.

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Chapter 6

Conclusions

6.1 *Conclusions*

A complete model of a binary concentration polarization layer within a dead-end filtration system has been derived within the framework of nonequilibrium thermodynamics (Chapters 2 and 3). The model contains a constitutive equation relating the mass diffusive flux to concentration gradients and pressure gradients within the layer, as well as a system of partial differential equations describing the pressure and concentration as functions of position and time. The complete model describes all concentration polarization phenomena, regardless of the physical properties of the molecules within the layer. The constitutive relation is seen to reduce to several equations which have been traditionally used in the study of concentration polarization (Fick's law, Darcy's law, Shirato equation, modified Darcy's law) as limiting cases. All assumptions have been carefully recorded and the equations obtained have been proven to be equivalent to equations from other works where possible. All mathematic and thermodynamic identities used in the theoretical development have been derived in appendices.

A brief review chapter has been included in an attempt to provide clarification regarding some uncertainty in the literature as to the nature of a macromolecular concentration polarization layer (Chapter 4). The chapter contains a summary of an early paper [Kozinski, 1972] which recognized that essentially the same phenomena occur in all concentration polarization layers, the most general case being a macromolecular system, which contains properties of a diffusion layer (*i.e.* Brownian diffusion processes) and properties of a porous medium (*i.e.* pressure gradients) simultaneously. Also included is a critique of several theorems [Dejmek, 1975; Wales, 1981; Wijmans, 1985; Johnson, 1987; Jonsson, 1996], some of which appear to prove that pressure gradients cannot exist within macromolecular concentration polarization layers, in contradiction to the above view. It is seen that these theorems all contain essentially the same error (using equations in their development that are only valid within systems at constant pressure) which makes them invalid.

The theoretical results have been applied to several experimental systems from the literature (Chapter 5). A relation between the diffusion coefficient and the sedimentation coefficient, sometimes called the *generalized Stokes-Einstein relation* [Bowen, 1998], has been tested, using experimental data for the protein bovine serum albumin (BSA); given that the experimental data were not obtained under identical ionic conditions, the prediction appears to be adequate. Some results obtained by various authors [Vilker, 1981; Boulanouar, 1996; Bowen, 1996] in the study of BSA concentration polarization layers were reviewed and it was concluded that both Brownian diffusion processes and pressure gradients were likely present within the layer. Some anomalous BSA permeability predictions [Kim, 1991] were explained by the fact that the modified Darcy's law was used within a system to which it did not apply. An experimental system appearing to provide evidence that pressure gradients were negligible within a BSA concentration polarization layer [Kim, 1991] was studied. It was concluded that adsorption and fouling of the membrane may have increased the resistance of the membrane to the point where any pressure variations across the layer were negligible relative to the overall driving pressure. An experimental study of a concentration polarization layer containing the biopolymer hyaluronate (HA) [Gowman, 1996] was reviewed, as it contained evidence for the existence of both Brownian diffusion processes and pressure gradients within the layer. Using the modified Darcy's law, the steady state pressure profile within the system was predicted. The result agreed with recent experiments [Ethier, 1999] showing the pressure variations across the layer to be negligible relative to the overall driving pressure. It was concluded that considerable adsorption and fouling of the membrane occurred within the HA system as well, making the pressure variations across the layer insignificant relative to the overall driving pressure.

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Appendix A: Proofs and Derivations

At different places in this work, we have noted when an equation is equivalent to an equation from another work or from another section of this work. For example, on page 21 we noted that equation (2.10) is equivalent to equation (II.13) on page 13 of **Non-Equilibrium Thermodynamics** [de Groot, 1962]. In that instance the two equations are almost identical (the only difference is that de Groot and Mazur denote the substantial derivative by $\frac{d}{dt}$, whereas we denote it by $\frac{D}{Dt}$); however, the equations are not always that similar. In this appendix, we will show that the equations are equivalent in the instances where it is not so obvious.

A.1 *Proof that equation (2.18) is equivalent to equation (18.3-3) of Transport Phenomena [Bird, 1960]*

In Appendix A.1, we will first show that equation (2.18) is equivalent to equation (18.3-3) on page 560 of **Transport Phenomena** [Bird, 1960] and then we will show that equation (2.18) reduces to equation (II.28) of **Non-Equilibrium Thermodynamics** [de Groot, 1962], if the body forces $\boldsymbol{F}_k$ are conservative.

First we will prove that equation (2.18) is equivalent to equation (18.3-3) on page 560 of **Transport Phenomena** [Bird, 1960], in the absence of effects due to viscosity. Equation (18.3-3) is, for a binary system,

$$\rho\frac{D}{Dt}\left\{\hat{U}+\frac{1}{2}\boldsymbol{v}^2\right\} = -(\nabla\cdot\boldsymbol{q})-(\nabla\cdot[\boldsymbol{\pi}\cdot\boldsymbol{v}])+(\boldsymbol{n}_A\cdot\boldsymbol{g}_A)+(\boldsymbol{n}_B\cdot\boldsymbol{g}_B). \tag{A.1}$$

Equation (16.1-5) on page 500 is

$$\boldsymbol{n}_i = \rho_i\boldsymbol{v}_i. \tag{A.2}$$

Using the relation $\pi = \tau + p\delta$ given in the paragraph just below equation (18.3-3), neglecting viscous effects ($\tau = 0$) and using equation (16.1-5), equation (18.3-3) can be written

$$\rho \frac{D}{Dt}\left(\hat{U} + \frac{1}{2}v^2\right) = -\nabla \cdot \boldsymbol{q} - \nabla \cdot p\boldsymbol{\delta} \cdot \boldsymbol{v} + \rho_A \boldsymbol{v}_A \cdot \boldsymbol{g}_A + \rho_B \boldsymbol{v}_B \cdot \boldsymbol{g}_B \,. \tag{A.3}$$

Equation (2.18) is

$$\rho \frac{De}{Dt} = -\nabla \cdot \boldsymbol{J}_e + \sigma_e \,. \tag{A.4}$$

Inserting equations (2.19) through (2.22) into equation (2.18) yields

$$\rho \frac{D}{Dt}\left(u + \frac{1}{2}v^2\right) = -\nabla \cdot \boldsymbol{J}_q - \nabla \cdot p\boldsymbol{U} \cdot \boldsymbol{v} + \rho_1 \boldsymbol{v}_1 \cdot \boldsymbol{F}_1 + \rho_2 \boldsymbol{v}_2 \cdot \boldsymbol{F}_2 \,. \tag{A.5}$$

The entries in Table A-1 can be used to convert equation (A.5) to the notation used in **Transport Phenomena** to yield

$$\rho \frac{D}{Dt}\left(\hat{U} + \frac{1}{2}v^2\right) = -\nabla \cdot \boldsymbol{q} - \nabla \cdot p\boldsymbol{\delta} \cdot \boldsymbol{v} + \rho_A \boldsymbol{v}_A \cdot \boldsymbol{g}_A + \rho_B \boldsymbol{v}_B \cdot \boldsymbol{g}_B \,. \tag{A.6}$$

Comparing equations (A.6) and (A.3), we see that equations (2.18) and (18.3-3) are equivalent when effects due to viscosity are neglected.

Table A-1

Notation used in this work	Notation used in Transport Phenomena
$\rho_k, \quad (k = 1, 2)$	$\rho_i, \quad (i = A, B)$
u	$\hat{U}$
$\boldsymbol{J}_q$	$\boldsymbol{q}$
$\boldsymbol{U}$	$\boldsymbol{\delta}$
$\boldsymbol{v}_k, \quad (k = 1, 2)$	$\boldsymbol{v}_i, \quad (i = A, B)$
$\boldsymbol{F}_k, \quad (k = 1, 2)$	$\boldsymbol{g}_i, \quad (i = A, B)$

Now we will prove that equation (2.18) reduces to equation (II.31) on page 17 of **Non-Equilibrium Thermodynamics** [de Groot, 1962], if the body forces $\boldsymbol{F}_k$ are conservative and viscous effects are neglected. Equation (II.31) of **Non-Equilibrium Thermodynamics** is

$$\frac{\partial \rho e}{\partial t} = -\nabla \cdot \boldsymbol{J}_e . \tag{A.7}$$

Equations (II.32), (II.33) and (II.35) are, respectively,

$$e = \frac{1}{2}\boldsymbol{v}^2 + \psi + u , \tag{A.8}$$

$$\boldsymbol{J}_e = \rho e \boldsymbol{v} + \boldsymbol{P} \cdot \boldsymbol{v} + \sum_k \psi_k \boldsymbol{J}_k + \boldsymbol{J}_q , \tag{A.9}$$

$$\boldsymbol{P} = p\boldsymbol{U} + \Pi . \tag{A.10}$$

Equation (II.16) is

$$\rho \frac{da}{dt} = \frac{\partial a\rho}{\partial t} + \nabla \cdot a\rho \boldsymbol{v} . \tag{A.11}$$

Inserting equations (II.32), (II.33) and (II.35) into (II.31), and using equation (II.16), yields, for a binary system in which viscous effects are negligible ($\Pi = 0$),

$$\rho \frac{d}{dt}\left(u + \frac{1}{2}\boldsymbol{v}^2 + \psi\right) = -\nabla \cdot (\boldsymbol{J}_q + p\boldsymbol{U} \cdot \boldsymbol{v} + \psi_1 \boldsymbol{J}_1 + \psi_2 \boldsymbol{J}_2) . \tag{A.12}$$

Equation (2.18) is

$$\rho \frac{De}{Dt} = -\nabla \cdot \boldsymbol{J}_e + \sigma_e . \tag{A.13}$$

Inserting equations (2.19) through (2.22) into equation (2.18), and using equation (2.11), yields

$$\rho \frac{D}{Dt}\left(u + \frac{1}{2}\boldsymbol{v}^2\right) = -\nabla \cdot \boldsymbol{J}_q - \nabla \cdot p\boldsymbol{U} \cdot \boldsymbol{v} + \boldsymbol{J}_1 \cdot \boldsymbol{F}_1 + \boldsymbol{J}_2 \cdot \boldsymbol{F}_2 + \rho_1 \boldsymbol{v} \cdot \boldsymbol{F}_1 + \rho_2 \boldsymbol{v} \cdot \boldsymbol{F}_2 \tag{A.14}$$

If the $\boldsymbol{F}_k$ are conservative, then they are defined by the relations

$$\boldsymbol{F}_k = -\nabla\psi_k, \quad (k = 1, 2), \tag{A.15}$$

$$\frac{\partial\psi_k}{\partial t} = 0, \quad (k = 1, 2), \tag{A.16}$$

where ψ_k is the potential per unit mass, independent of time, associated with $\boldsymbol{F}_k$. Using equations (A.15) and (A.16), the last two terms on the right hand side of equation (A.14) can be written

$$\rho_1\boldsymbol{v}\cdot\boldsymbol{F}_1 + \rho_2\boldsymbol{v}\cdot\boldsymbol{F}_2 = -\rho_1\left(\frac{\partial\psi_1}{\partial t} + \boldsymbol{v}\cdot\nabla\psi_1\right) - \rho_2\left(\frac{\partial\psi_2}{\partial t} + \boldsymbol{v}\cdot\nabla\psi_2\right). \tag{A.17}$$

Using equations (2.12) and (2.7), equation (A.17) may be written

$$\rho_1\boldsymbol{v}\cdot\boldsymbol{F}_1 + \rho_2\boldsymbol{v}\cdot\boldsymbol{F}_2 = -\rho c_1\frac{D\psi_1}{Dt} - \rho c_2\frac{D\psi_2}{Dt}. \tag{A.18}$$

Using the chain rule and equation (2.10), equation (A.18) may be written

$$\rho_1\boldsymbol{v}\cdot\boldsymbol{F}_1 + \rho_2\boldsymbol{v}\cdot\boldsymbol{F}_2 = -\rho\frac{D\psi}{Dt} - \psi_1\nabla\cdot\boldsymbol{J}_1 - \psi_2\nabla\cdot\boldsymbol{J}_2, \tag{A.19}$$

where ψ is the total specific potential energy of the mixture

$$\psi = c_1\psi_1 + c_2\psi_2. \tag{A.20}$$

Inserting equation (A.19) into (A.14) yields, using also equations (A.15), (B.13) and noting that the substantial derivative is denoted by d/dt in **Non-Equilibrium Thermodynamics**,

$$\rho\frac{d}{dt}\left(u + \frac{1}{2}v^2 + \psi\right) = -\nabla\cdot(\boldsymbol{J}_q + p\boldsymbol{U}\cdot\boldsymbol{v} + \psi_1\boldsymbol{J}_1 + \psi_2\boldsymbol{J}_2). \tag{A.21}$$

Comparing equations (A.21) and (A.12), we see that, for conservative body forces, equation (2.18) is equivalent to equation (II.31) of **Non-Equilibrium Thermodynamics** [de Groot, 1962], in the absence of viscous effects.

A.2 *Proof that equation (2.58) is equivalent to equation (18.3-1) of Transport Phenomena [Bird, 1960]*

In Appendix A.2, we will show that equation (2.58) of this work is equivalent to equation (F) of Table 18.3-1 on page 562 of **Transport Phenomena** [Bird, 1960]. Equation (F) is, for a binary system in the absence of chemical reactions and viscous effects,

$$\rho\hat{C}_p\frac{DT}{Dt} = -(\nabla\cdot\boldsymbol{q}) + (\boldsymbol{j}_A\cdot\boldsymbol{g}_A) + (\boldsymbol{j}_B\cdot\boldsymbol{g}_B) + \left(\frac{\partial\ln\hat{V}}{\partial\ln T}\right)_{p,x_i}\frac{Dp}{Dt}$$

$$+\overline{H}_A(\nabla\cdot\boldsymbol{J}_A) + \overline{H}_B(\nabla\cdot\boldsymbol{J}_B)\,. \qquad \text{(A.22)}$$

Equation (2.58) is

$$T\alpha_p\frac{Dp}{Dt} - \rho c_p\frac{DT}{Dt} = \nabla\cdot\boldsymbol{J}_q - \boldsymbol{J}_1\cdot\boldsymbol{F}_1 - \boldsymbol{J}_2\cdot\boldsymbol{F}_2 - h_1\nabla\cdot\boldsymbol{J}_1 - h_2\nabla\cdot\boldsymbol{J}_2\,. \qquad \text{(A.23)}$$

The coefficient of thermal expansion α_p is defined by equation (C.20):

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,M_k}, \qquad \text{(A.24)}$$

where V is the volume of a mass element in local equilibrium, and the subscript M_k indicates that the component masses are held constant. Equation (A.24) may be differentiated to yield

$$\alpha_p = \frac{1}{T}\left(\frac{\partial\ln\upsilon}{\partial\ln T}\right)_{p,M_k}; \qquad \text{(A.25)}$$

or, equivalently,

$$\alpha_p = \frac{1}{T}\left(\frac{\partial\ln\upsilon}{\partial\ln T}\right)_{p,x_k}, \qquad \text{(A.26)}$$

where υ is the specific volume:

$$\upsilon = \frac{V}{M}, \tag{A.27}$$

and the subscript x_k indicates that the component mole fractions are held constant. Inserting equation (A.26) into equation (A.23), and rearranging, yields

$$\rho c_p \frac{DT}{Dt} = -\nabla \cdot \boldsymbol{J}_q + \boldsymbol{J}_1 \cdot \boldsymbol{F}_1 + \boldsymbol{J}_2 \cdot \boldsymbol{F}_2 + \left(\frac{\partial \ln \upsilon}{\partial \ln T}\right)_{p,\, x_k} \frac{Dp}{Dt} + h_1 \nabla \cdot \boldsymbol{J}_1 + h_2 \nabla \cdot \boldsymbol{J}_2 . \tag{A.28}$$

The entries in Table A-2 may be used to convert equation (A.28) to the notation used in **Transport Phenomena** to yield

$$\rho \hat{C}_p \frac{DT}{Dt} = -(\nabla \cdot \boldsymbol{q}) + (\boldsymbol{j}_A \cdot \boldsymbol{g}_A) + (\boldsymbol{j}_B \cdot \boldsymbol{g}_B) + \left(\frac{\partial \ln \hat{V}}{\partial \ln T}\right)_{p,\, x_i} \frac{Dp}{Dt}$$

$$+\overline{H}_A(\nabla \cdot \boldsymbol{J}_A) + \overline{H}_B(\nabla \cdot \boldsymbol{J}_B) . \tag{A.29}$$

Comparing equations (A.29) and (A.22), we see that equations (2.58) and (F) are equivalent, in the absence of chemical reactions and viscous effects.

Table A-2

Notation used in this work	**Notation used in Transport Phenomena**
c_p	$\hat{C}_p$
$\boldsymbol{J}_q$	$\boldsymbol{q}$
$\boldsymbol{J}_k, \quad (k = 1, 2)$	$\boldsymbol{j}_i, \quad (i = A, B)$
$\boldsymbol{J}_k, \quad (k = 1, 2)$	$M_i \boldsymbol{J}_i, \quad (i = A, B)$
$\boldsymbol{F}_k, \quad (k = 1, 2)$	$\boldsymbol{g}_i, \quad (i = A, B)$
υ	$\hat{V}$
$h_k, \quad (k = 1, 2)$	$\overline{H}_i / M_i, \quad (i = A, B)$

A.3 *Proof that equation (2.75) is equivalent to equation (72) of Hooyman et al. [1953]*

In Appendix A.3, we will show that equation (2.75) of this work is equivalent to equation (72) on page 1105 of the paper by Hooyman, Holton, Mazur and de Groot [1953]. Equation (72) of Hooyman *et al.*'s paper is

$$L = \omega_2^2 \rho_2 c_2^{-1} \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}^{-1} D. \tag{A.30}$$

Equation (2.75) of our work is

$$L = c_2 \rho \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}^{-1} D \quad . \tag{A.31}$$

All of the factors appearing in equations (A.30) and (A.31) are defined in the same manner except for the quantity ω_2, a weighting factor which depends on the reference system being used, appearing in (A.30). In the present work, we have defined the diffusional flows with respect to the barycentric velocity $\boldsymbol{v}$, in which case $\omega_2 = c_2$ [Hooyman, 1953, page 1104]; thus, for the reference system used in this work, equation (A.30) may be written

$$L = c_2 \rho \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}^{-1} D \quad . \tag{A.32}$$

Comparing equations (A.32) and (A.31), we see that equation (2.75) of this work is equivalent to equation (72) of the paper by Hooyman *et al.* [1953].

A.4 *Proof that equation (2.76) is equivalent to equation (18.4-14) of Transport Phenomena*

In Appendix A.4, we will show that equation (2.76) is equivalent to equation (18.4-14) on page 568 of **Transport Phenomena** [Bird, 1960] and equation (11.2-54) on page 718 of the **Molecular Theory of Gases and Liquids** [Hirschfelder, 1954]. Since equations (2.76) and (2.81) are equivalent, the results of this appendix also apply to equation (2.81). Equation (18.4-14) of **Transport Phenomena** is, in the absence of temperature gradients,

$$j_A = -\left(\frac{c^2}{\rho RT}\right)M_A^{\,2}M_B D_{AB}x_A \cdot \left[\left(\frac{\partial}{\partial x_A}\frac{\bar{G}_A}{M_A}\right)_{T,p}\nabla x_A - \frac{\rho_B}{\rho}(g_A - g_B) + \left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right)\nabla p\right]. \tag{A.33}$$

The coefficient D_{AB} appearing in equation (A.33) may be replaced by the binary diffusion coefficient $\mathcal{D}_{AB}$ by comparing with Fick's law. In the absence of pressure gradients and external body forces, equation (A.33) may be written

$$j_A = -\left(\frac{c^2}{\rho RT}\right)M_A^{\,2}M_B D_{AB}x_A\left(\frac{\partial}{\partial x_A}\frac{\bar{G}_A}{M_A}\right)_{T,p}\nabla x_A \;. \tag{A.34}$$

Equation (18.4-17), Fick's law, is

$$j_A = -\left(\frac{c^2}{\rho}\right)M_A M_B \mathcal{D}_{AB}\nabla x_A \,. \tag{A.35}$$

Comparing equation (A.35) with (A.34) yields a relation between $\mathcal{D}_{AB}$ and D_{AB}:

$$\mathcal{D}_{AB} = \frac{M_A x_A}{RT}D_{AB}\left(\frac{\partial}{\partial x_A}\frac{\bar{G}_A}{M_A}\right)_{T,p} . \tag{A.36}$$

Inserting equation (A.36) into (A.33) yields

$$j_A = -\left(\frac{c^2}{\rho}\right)M_A M_B\left(\frac{\partial}{\partial x_A}\frac{\bar{G}_A}{M_A}\right)_{T,p}^{-1}\mathcal{D}_{AB}\left[\left(\frac{\partial}{\partial x_A}\frac{\bar{G}_A}{M_A}\right)_{T,p}\nabla x_A - \frac{\rho_B}{\rho}(g_A - g_B) + \left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right)\nabla p\right]. \tag{A.37}$$

Equation (A.37) may be written in terms of mass fractions using entry (N) of Table 16.1-1 on page 498 of **Transport Phenomena**:

$$dx_A = \frac{d\omega_A}{M_A M_B\left(\frac{\omega_A}{M_A} + \frac{\omega_B}{M_B}\right)^2}. \tag{A.38}$$

Entries (B), (C) and (D) of the same table are, respectively,

$$\rho_A = c_A M_A, \tag{A.39}$$

$$\omega_A = \frac{\rho_A}{\rho}, \tag{A.40}$$

$$c = c_A + c_B. \tag{A.41}$$

Using equations (A.39), (A.40) and (A.41), equation (A.38) may be written

$$dx_A = \frac{\rho^2}{c^2 M_A M_B} d\omega_A. \tag{A.42}$$

Using equation (A.42), equation (A.37) may be written

$$\boldsymbol{j}_A = -\rho\left(\frac{\partial}{\partial\omega_A}\frac{\overline{G}_A}{M_A}\right)^{-1}_{T,p} \mathscr{D}_{AB}\left[\left(\frac{\partial}{\partial\omega_A}\frac{\overline{G}_A}{M_A}\right)_{T,p} \nabla\omega_A - \frac{\rho_B}{\rho}(\boldsymbol{g}_A - \boldsymbol{g}_B) + \left(\frac{\overline{V}_A}{M_A} - \frac{1}{\rho}\right)\nabla p\right] \tag{A.43}$$

Equation (2.76) is

$$\boldsymbol{J}_1 = -c_2\rho\left(\frac{\partial\mu_1}{\partial c_1}\right)^{-1}_{T,p} D(\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2). \tag{A.44}$$

At constant temperature, the Gibbs-Duhem relation, equation (C.38), may be written

$$\rho_1\nabla_T\mu_1 + \rho_2\nabla_T\mu_2 = \nabla p. \tag{A.45}$$

Inserting equation (A.45) into equation (A.44) yields, using also equations (2.7) and (2.8),

$$\boldsymbol{J}_1 = -\rho\left(\frac{\partial\mu_1}{\partial c_1}\right)^{-1}_{T,p} D\left[\nabla_T\mu_1 - \frac{\rho_2}{\rho}(\boldsymbol{F}_1 - \boldsymbol{F}_2) - \frac{1}{\rho}\nabla p\right]. \tag{A.46}$$

In a binary system at constant temperature, a chemical potential gradient can be written, using equation (C.66),

$$\nabla_T \mu_1 = \upsilon_1 \nabla p + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \nabla c_1, \tag{A.47}$$

Inserting (A.47) into (A.46) yields

$$\boldsymbol{J}_1 = -\rho\left(\frac{\partial \mu_1}{\partial c_1}\right)^{-1}_{T,p} D\left[\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \nabla c_1 - \frac{\rho_2}{\rho}(\boldsymbol{F}_1 - \boldsymbol{F}_2) + \left(\upsilon_1 - \frac{1}{\rho}\right)\nabla p\right]. \tag{A.48}$$

The entries in Table A-3 can be used to convert equation (A.48) to the notation used in **Transport Phenomena**. Equation (A.48) then becomes

$$\boldsymbol{j}_A = -\rho\left(\frac{\partial}{\partial \omega_A}\frac{\overline{G}_A}{M_A}\right)^{-1}_{T,p} \mathscr{D}_{AB}\left[\left(\frac{\partial}{\partial \omega_A}\frac{\overline{G}_A}{M_A}\right)_{T,p} \nabla \omega_A - \frac{\rho_B}{\rho}(\boldsymbol{g}_A - \boldsymbol{g}_B) + \left(\frac{\overline{V}_A}{M_A} - \frac{1}{\rho}\right)\nabla p\right]. \tag{A.49}$$

Comparing equations (A.49) and (A.43), we see that equations (2.76) and (18.4-14) are equivalent, in the absence of temperature gradients.

Table A-3

Notation used in this work	**Notation used in Transport Phenomena**
$\boldsymbol{J}_k$, $(k = 1, 2)$	$\boldsymbol{j}_i$, $(i = A, B)$
$c_k = \rho_k/\rho$, $(k = 1, 2)$	$\omega_i = \rho_i/\rho$, $(i = A, B)$
ρ_k, $(k = 1, 2)$	ρ_i, $(i = A, B)$
υ_k, $(k = 1, 2)$	$\overline{V}_i/M_i$, $(i = A, B)$
μ_k, $(k = 1, 2)$	$\overline{G}_i/M_i$, $(i = A, B)$
D	$\mathscr{D}_{AB}$
$\boldsymbol{F}_k$, $(k = 1, 2)$	$\boldsymbol{g}_i$, $(i = A, B)$

Next we will prove that equation (11.2-54) of the **Molecular Theory of Gases and Liquids** is equivalent to equation (18.4-14) of **Transport Phenomena**, thereby proving equivalence to equations (2.76) and (2.81) as well. Equation (11.2-54) is, in the absence of temperature gradients,

$$\sum_j \frac{n_i n_j}{n^2 \mathcal{D}_{ij}} (\bar{V}_j - \bar{V}_i) = d_i . \tag{A.50}$$

For a binary system, $\mathcal{D}_{ii} = 0$ and equation (A.50) may be written

$$\frac{n_1 n_2}{n^2 \mathcal{D}_{12}} (\bar{V}_2 - \bar{V}_1) = d_1 . \tag{A.51}$$

From page 709 of the **Molecular Theory of Gases and Liquids** we obtain the definition

$$j_i = n_i m_i \bar{V}_i , \tag{A.52}$$

and from page 454 we obtain

$$\bar{V}_i = \bar{v}_i - v_0 , \tag{A.53}$$

$$v_0 = \frac{n_1 m_1}{\rho} \bar{v}_1 + \frac{n_2 m_2}{\rho} \bar{v}_2 , \tag{A.54}$$

$$\rho = n_1 m_1 + n_2 m_2 . \tag{A.55}$$

Using equations (A.52) to (A.55), equation (A.51) may be written

$$-\frac{\rho}{m_1 m_2} \frac{j_1}{n^2 \mathcal{D}_{12}} = d_1 . \tag{A.56}$$

Equation (11.2-29) on page 714 may be written, for a binary system,

$$d_1 = \frac{n_1}{nkT} \left[\left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,p} \frac{\partial x_1}{\partial r} + \left(\bar{V}_1 - \frac{m_1}{\rho} \right) \frac{\partial p}{\partial r} - \left(X_1 - \frac{m_1}{\rho} n_1 X_1 - \frac{m_1}{\rho} n_2 X_2 \right) \right] . \tag{A.57}$$

From page 1181 we obtain

$$R = \tilde{N} k . \tag{A.58}$$

Combining equations (A.56) and (A.57), and using equations (A.55) and (A.58), yields

$$j_1 = -\left(\frac{n}{\tilde{N}}\right)^2\frac{(m_1\tilde{N})^2(m_2\tilde{N})}{\rho RT}\mathcal{D}_{12}\frac{n_1}{n}\left[\left(\frac{\partial}{\partial x_1}\frac{\mu_1}{m_1}\right)_{T,p}\frac{\partial x_1}{\partial r}+\left(\frac{\overline{V}_1}{m_1}-\frac{1}{\rho}\right)\frac{\partial p}{\partial r}\right.$$

$$\left.-\frac{m_2 n_2}{\rho}\left(\frac{X_1}{m_1}-\frac{X_2}{m_2}\right)\right]. \quad (A.59)$$

The entries in Table A-4 may be used to convert equation (A.59) to the notation used in **Transport Phenomena**. Equation (A.59) then becomes

$$j_A = -\left(\frac{c^2}{\rho RT}\right)M_A{}^2 M_B D_{AB} x_A\left[\left(\frac{\partial}{\partial x_A}\frac{\overline{G}_A}{M_A}\right)_{T,p}\nabla x_A+\left(\frac{\overline{V}_A}{M_A}-\frac{1}{\rho}\right)\nabla p-\frac{\rho_B}{\rho}(g_A-g_B)\right]. \quad (A.60)$$

Comparing equations (A.60) and (A.33), we see that equation (11.2-54) of the **Molecular Theory of Gases and Liquids** is equivalent to equation (18.4-14) of **Transport Phenomena**, and therefore equivalent to equations (2.76) and (2.81) as well.

Table A-4

Notation used in Transport Phenomena	Notation used in Molecular Theory...
j_i, $(i = A, B)$	j_i, $(i = 1, 2)$
M_i, $(i = A, B)$	$m_i\tilde{N}$, $(i = 1, 2)$
ρ_i, $(i = A, B)$	$n_i m_i$, $(i = 1, 2)$
$\overline{V}_i/M_i$, $(i = A, B)$	$\overline{V}_i/m_i$, $(i = 1, 2)$
$\overline{G}_i/M_i$, $(i = A, B)$	μ_i/m_i, $(i = 1, 2)$
D_{AB}	$\mathcal{D}_{12}$
g_i, $(i = A, B)$	X_i/m_i, $(i = 1, 2)$
x_i, $(i = A, B)$	$x_i = n_i/n$, $(i = 1, 2)$
c	$n/\tilde{N}$
∇	$\partial/\partial r$

A.5 *Proof that equation (2.93) is equivalent to equation (14) of Mijnlieff and Jaspers [1971]*

In Appendix A.5, we will show that equation (2.93) of this work is equivalent to equation (14) on page 1841 of the paper by Mijnlieff and Jaspers [1971]. Equation (14) of Mijnlieff and Jaspers' paper is

$$k = \left(\frac{\rho\upsilon_0}{c_1}\right)^2 Q\eta_0 . \tag{A.61}$$

Equation (2.93) of our work is

$$L = \left(\frac{c_2}{\upsilon_1}\right)^2 \frac{k}{\eta_1} . \tag{A.62}$$

Rearranging equation (A.62) for the permeability k yields, using also equation (2.7),

$$k = \left(\frac{\rho\upsilon_1}{\rho_2}\right)^2 L\eta_1 . \tag{A.63}$$

By inserting the relations in Table A-5 we may convert equation (A.63) into the notation used by Mijnlieff and Jaspers to yield

$$k = \left(\frac{\rho\upsilon_0}{c_1}\right)^2 Q\eta_0 . \tag{A.64}$$

Comparing equations (A.64) and (A.61) we see that equation (2.93) of the present work is equivalent to equation (14) of Mijnlieff and Jaspers' paper.

Table A-5

Notation used in this work	Notation used by Mijnlieff
$\upsilon_k, \quad (k = 1, 2)$	$\upsilon_i, \quad (i = 0, 1)$
$\rho_k, \quad (k = 1, 2)$	$c_i, \quad (i = 0, 1)$
L	Q

Table A-5

Notation used in this work	Notation used by Mijnlieff
η_1	η_0
$\tilde{s}$	s_1

A.6 *Proof that equation (2.107) is equivalent to equation (12) of Mijnlieff and Jaspers [1970]*

In Appendix A.6, we will show that equation (2.107) is equivalent to equation (12) on page 1840 of the paper by Mijnlieff and Jaspers [1970]. Equation (12) of Mijnlieff and Jaspers' paper is

$$s_1 = Q\frac{\rho\upsilon_0}{c_1}\left(1+\frac{c_1}{c_0}\right)(1-\rho\upsilon_1). \tag{A.65}$$

Equation (5) of their paper is

$$\rho = c_0 + c_1. \tag{A.66}$$

Using equation (5), equation (A.65) can be written

$$s_1 = Q\frac{\rho^2\upsilon_0}{c_0c_1}(1-\rho\upsilon_1). \tag{A.67}$$

Equation (2.107) is

$$L = \frac{c_1c_2}{\upsilon_1(1-\rho\upsilon_2)}\tilde{s}. \tag{A.68}$$

Rearranging for $\tilde{s}$ and using equation (2.7), equation (A.68) can be written

$$\tilde{s} = L\frac{\rho^2\upsilon_1}{\rho_1\rho_2}(1-\rho\upsilon_2). \tag{A.69}$$

Using the relations in Table A-5 to convert equation (A.69) from the notation used in this work to the notation used by Mijnlieff and Jaspers yields

$$s_1 = Q\frac{\rho^2 \upsilon_0}{c_0 c_1}(1 - \rho\upsilon_1). \tag{A.70}$$

Comparing equations (A.70) and (A.67) we see that equation (2.107) of this work is equivalent to equation (12) of the paper by Mijnleiff and Jaspers.

A.7 *Proof that equation (2.111) reduces to the Svedberg equation*

In Appendix A.7, we will show that, for a dilute macromolecular solution, equation (2.111) reduces to the Svedberg equation of ultracentrifugation. The Svedberg equation, equation (3a) of **The Ultracentrifuge** [Svedberg, 1940], is

$$M = \frac{RTs}{D(1 - V\rho)}. \tag{A.71}$$

Equation (2.111) is, using equation (2.9),

$$D = \frac{-c_1}{\rho\upsilon_1(1 - \rho\upsilon_2)}\left(\frac{\partial\mu_1}{\partial c_2}\right)_{T,p}\tilde{s}. \tag{A.72}$$

We can convert the mass fraction partial derivative ∂c_2 in equation (A.72) to a mole fraction partial derivative ∂x_2 using the definition

$$x_2 = \frac{c_2/\mathcal{M}_2}{c_1/\mathcal{M}_1 + c_2/\mathcal{M}_2}, \tag{A.73}$$

where $\mathcal{M}_k$ is the molar mass of the k^{th} component. Differentiating equation (A.73) yields, using equation (2.9),

$$\partial x_2 = \frac{\partial x_2}{\partial c_1}\partial c_1 + \frac{\partial x_2}{\partial c_2}\partial c_2 = \frac{\partial c_2}{\mathcal{M}_1\mathcal{M}_2(c_1/\mathcal{M}_1 + c_2/\mathcal{M}_2)^2}. \tag{A.74}$$

For very dilute solutions containing macromolecular solutes, $c_2/\mathcal{M}_2$ can be neglected and equation (A.74) can be rearranged to yield

$$\partial c_2 = \frac{\mathcal{M}_2 c_1^2}{\mathcal{M}_1}\partial x_2 . \qquad \text{(A.75)}$$

Inserting equation (A.75) into (A.72) yields, using equation (2.7),

$$D = \frac{-\mathcal{M}_1}{\mathcal{M}_2 \rho_1 \upsilon_1 (1-\rho\upsilon_2)}\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p}\tilde{s} . \qquad \text{(A.76)}$$

For very dilute solutions, the chemical potential of the solvent may be written [Callen, 1985, p303] (see footnote 14 on page 28)

$$\mathcal{M}_1 \mu_1(T,p,x_2) = \mathcal{M}_1 \mu_1^0(T,p) - RTx_2 , \qquad \text{(A.77)}$$

where μ_1^0 is the chemical potential of pure solvent and R is the universal gas constant; also, for dilute solutions, the solvent partial specific volume may be set equal to the inverse of the solvent density

$$\upsilon_1 = \rho_1^{-1} ; \qquad \text{(A.78)}$$

Equation (A.77) can be differentiated to obtain

$$\mathcal{M}_1\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,p} = -RT . \qquad \text{(A.79)}$$

Inserting equations (A.79) and (A.78) into (A.76), and rearranging for $\mathcal{M}_2$, yields

$$\mathcal{M}_2 = \frac{RT\tilde{s}}{D(1-\rho\upsilon_2)} . \qquad \text{(A.80)}$$

We can now use the relations in Table A-6 to convert equation (A.80) from the notation used in this work to the notation used by Svedberg [1940] to yield

$$M = \frac{RTs}{D(1-V\rho)} . \qquad \text{(A.81)}$$

Comparing equations (A.81) and (A.71), we see that, for a dilute macromolecular solution, equation (2.111) reduces to the Svedberg equation of ultracentrifugation.

Table A-6

Notation used in this work	**Notation used by Svedberg**
m_2	M
υ_2	V
$\tilde{s}$	s

A.8 *Proof that Equation (3.6) is equivalent to equation (7) of Kozinski and Lightfoot [1972]*

In Appendix A.8, we will show that equation (3.6) is equivalent to equation (7) of Kozinski and Lightfoot's [1972] paper. Kozinski and Lightfoot obtained equation (7) of their paper by applying the boundary conditions of an ultrafiltration experiment to their equations (1) and (2), the Stefan-Maxwell equations. However, the equations in Kozinski and Lightfoot's paper contain several typographical errors which make it difficult to follow their derivation; therefore, before proving the equivalence of equations (7) and (3.6), we will derive equation (7) from equations (1) and (2), and point out the typographical errors, for the sake of clarity. Equations (1) and (2) of their paper are

$$\boldsymbol{d}_i = \sum_{j=1, j \neq i}^{m} \frac{X_i X_j}{D_{ij}} (\boldsymbol{V}_j - \boldsymbol{V}_i) = \sum_{j=1, j \neq i}^{m} \frac{1}{C_m D_{ij}} (X_i \boldsymbol{N}_j - X_j \boldsymbol{N}_i), \tag{A.82}$$

$$\boldsymbol{d}_i = \frac{X_i}{RT} \nabla_{T,P} \tilde{\mu}_i + \left(\frac{X_i \bar{V}_i}{RT} - \frac{\tilde{\omega}_i}{C_m RT} \right) \nabla P - \frac{\rho_i}{C_m RT} \left[\boldsymbol{g}_i - \sum_{k=1}^{m} \tilde{\omega}_k \boldsymbol{g}_k \right], \tag{A.83}$$

where X_i is the mole fraction of the i^{th} component; D_{ij} is a phenomenological coefficient; $\boldsymbol{V}_i$ is the local velocity of the i^{th} component; C_m is the total molar concentration; $\boldsymbol{N}_i$ is the molar flux of the i^{th} component:

$$\boldsymbol{N}_i = X_i C_m \boldsymbol{V}_i; \tag{A.84}$$

R is the universal gas constant; T is the temperature; P is the pressure; $\tilde{\mu}_i$ is the chemical potential of the i^{th} component; $\bar{V}_i$ is the partial molar volume of the i^{th} component; $\tilde{\omega}_i$ is the mass fraction of the i^{th} component; ρ_i is the mass density of the i^{th} component; and, $\mathbf{g}_i$ is the total body force per unit mass acting on the i^{th} component.[1]

For a binary system, equations (A.82) and (A.83) may be combined to yield

$$\frac{RT}{C_m D_{ps}}(X_s N_p - X_p N_s) = X_s \nabla_{T,P}\tilde{\mu}_s + \left(X_s \bar{V}_s - \frac{\tilde{\omega}_s}{C_m}\right)\nabla P - \frac{\rho_s}{C_m}[\mathbf{g}_s - \tilde{\omega}_s \mathbf{g}_s - \tilde{\omega}_p \mathbf{g}_p], \quad \text{(A.85)}$$

where the subscripts s and p signifiy the solvent and solute, respectively; and, the relation $D_{ps} = D_{sp}$ was used. Using the relations

$$X_s + X_p = 1 \quad \text{(A.86)}$$

and

$$\tilde{\omega}_s + \tilde{\omega}_p = 1, \quad \text{(A.87)}$$

equation (A.85) may be written

$$N_s - X_s(N_p + N_s) = -\frac{C_m D_{ps}}{RT}\left\{X_s \nabla_{T,P}\tilde{\mu}_s + \left(X_s \bar{V}_s - \frac{\tilde{\omega}_s}{C_m}\right)\nabla P - \frac{\rho_s \tilde{\omega}_p}{C_m}[\mathbf{g}_s - \mathbf{g}_p]\right\}. \quad \text{(A.88)}$$

---

[1] Note that the terms in the first parentheses of equation (A.83) are written $\left(X_i \bar{V}_i - \frac{\tilde{\omega}_i}{C_m RT}\right)$ in Kozinski and Lightfoot's paper. This is a typographical error, as they should be written as in equation (A.83). The Stefan-Maxwell equations are written correctly by Lightfoot in **Transport Phenomena and Living Systems** [1974] (equation (1.2.12) on page 161).

Let us write only the y-component of equation (A.88):

$$N_{sy} - X_s(N_{py} + N_{sy}) = -\frac{C_m D_{ps}}{RT}\left\{X_s\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)_{T,P}\right.$$

$$\left. + \left(X_s \bar{V}_s - \frac{\tilde{\omega}_s}{C_m}\right)\frac{\partial P}{\partial y} - \frac{\rho_s \tilde{\omega}_p}{C_m}[g_{sy} - g_{py}]\right\}. \quad \text{(A.89)}$$

The body forces acting within the concentration polarization layer are given by equations (5) and (6) of Kozinski and Lightfoot's paper:

$$g_{sy} = g_y, \quad \text{(A.90)}$$

$$g_{py} = g_y + \frac{1}{\rho_p}\frac{\partial P}{\partial y}, \quad \text{(A.91)}$$

where g_y is the y-component of the acceleration due to gravity.[2] Inserting equations (A.90) and (A.91) into (A.89) yields, using the relation $\tilde{\omega}_i = \rho_i / \rho$,

$$N_{sy} - X_s(N_{py} + N_{sy}) = -\frac{C_m D_{ps}}{RT}\left[X_s\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)_{T,P} + X_s \bar{V}_s \frac{\partial P}{\partial y}\right]. \quad \text{(A.92)}$$

Equation (A.92) is equation (7) of Kozinski and Lightfoot's paper.[3]

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[2] Note that equation (6) of Kozinski and Lightfoot's paper is written $g_{py} = g_y + \frac{1}{\rho}\frac{\partial P}{\partial y}$. This is another typographical error, as it should be written as in equation (A.91).

[3] Note that equation (7) of Kozinski and Lightfoot's paper, $N_{sy} - X_s(N_{py} - N_{sy}) = -\frac{C_m D_{ps}}{RT}\left[X_s \frac{\partial}{\partial y}\tilde{\mu}_s + X_s \bar{V}_s \frac{\partial P}{\partial y}\right]$, contains two more typographical errors. The left hand side of this equation contains a sign error and the right hand side implies the gradient of the full chemical potential $\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)$ rather than the gradient of the concentration-dependent part of the chemical potential $\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)_{T,P}$.

Let us now prove that equation (7) is equivalent to equation (3.6) of this work. Using equations (A.86) and (A.84), equation (A.92) can be written

$$(V_{sy} - V_{py}) = -\frac{D_{ps}}{X_p RT}\left[\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)_{T,P} + \bar{V}_s \frac{\partial P}{\partial y}\right]. \tag{A.93}$$

Equation (3.6) is

$$J_1 = -\frac{L}{c_2}\nabla_T \mu_1. \tag{A.94}$$

Using equations (2.11), (2.9), (2.6) and (C.66), the y-component of equation (A.94) may be written

$$(v_{1y} - v_{2y}) = -\frac{\rho}{\rho_1 \rho_2}\frac{L}{c_2}\left[\left(\frac{\partial \mu_1}{\partial y}\right)_{T,P} + \upsilon_1 \frac{\partial P}{\partial y}\right]. \tag{A.95}$$

We may use the relations in Table A-7 to convert equation (A.95) into the notation used by Kozinski and Lightfoot to yield

$$(V_{sy} - V_{py}) = -\frac{D_{ps}}{X_p RT}\left[\left(\frac{\partial \tilde{\mu}_s}{\partial y}\right)_{T,P} + \bar{V}_s \frac{\partial P}{\partial y}\right]. \tag{A.96}$$

Comparing equations (A.96) and (A.93), we see that equation (3.6) is equivalent to equation (7) of the paper by Kozinski and Lightfoot [1972].

Table A-7

Notation used in this work	**Notation used by Kozinski**
v_{ky}, $(k = 1, 2)$	V_{iy}, $(i = s, p)$
μ_k, $(k = 1, 2)$	$\tilde{\mu}_i / M_i$, $(i = s, p)$
υ_k, $(k = 1, 2)$	$\bar{V}_i / M_i$, $(i = s, p)$
p	P
ρ_k, $(k = 1, 2)$	$C_m X_i M_i$, $(i = s, p)$

Table A-7

Notation used in this work	**Notation used by Kozinski**
c_k, $(k = 1, 2)$	$\tilde{\omega}_i$, $(i = s, p)$
L	$\tilde{\omega}_p\left(\frac{C_m^2}{\rho RT}\right)M_s^2 M_p D_{ps} X_s$ [a]

---

a. This relation was obtained by comparing Section 2.4 of this work with Section 1.2 of **Transport Phenomena and Living Systems** [Lightfoot, 1974]. Note that D_{ps} is equivalent to D_{AB} used in equation (18.4-14) of **Transport Phenomena** [Bird, 1960].

A.9 *Proof that equation (3.10) reduces to the Shirato equation*

In Appendix A.9, we will show that, if the solute particles are large enough that Brownian diffusion may be neglected, equation (3.10) reduces to the Shirato equation of compressible cake filtration [Shirato, 1969]. The Shirato equation may be written [Tiller, 1975, equation (4.3), page 350]

$$\frac{dp_s}{dx} = -\frac{\mu}{K}(q - er). \tag{A.97}$$

In the absence of Brownian diffusion ($D = 0$), equation (3.10) may be written

$$J_1 = -\frac{c_2}{\upsilon_1}\frac{k}{\eta_1}\nabla p. \tag{A.98}$$

Using equation (2.78) and rearranging equation (A.98) for the pressure gradient yields

$$\nabla p = -\frac{\eta_1}{k}\left(\rho_1\upsilon_1\boldsymbol{v}_1 - \left(\frac{\rho_1\upsilon_1}{\rho_2\upsilon_2}\right)\rho_2\upsilon_2\boldsymbol{v}_2\right). \tag{A.99}$$

For a one-dimensional system we may write

$$\boldsymbol{v}_1 = v_1\hat{i}, \quad \boldsymbol{v}_2 = v_2\hat{i} \quad \text{and} \quad \nabla p = \frac{dp}{dx}\hat{i}, \tag{A.100}$$

and equation (A.99) may be written

$$\frac{dp}{dx} = -\frac{\eta_1}{k}\left(\rho_1\upsilon_1\nu_1 - \left(\frac{\rho_1\upsilon_1}{\rho_2\upsilon_2}\right)\rho_2\upsilon_2\nu_2\right). \tag{A.101}$$

The entries in Table A-8 may be used to convert equation (A.101) to the notation used by Tiller [1975] to yield

$$\frac{dp_s}{dx} = -\frac{\mu}{K}(q - er). \tag{A.102}$$

Comparing equations (A.102) and (A.97), we see that equation (3.10) reduces to the Shirato equation, in the absence of Brownian diffusion.

Table A-8

Notation used in this work	Notation used by Tiller
p	p_s
η_1	μ
k	K
$\rho_1\upsilon_1\nu_1$	q
$\rho_2\upsilon_2\nu_2$	r
$\rho_1\upsilon_1/\rho_2\upsilon_2$	e

A.10 *Proof that equation (4.12) reduces to equation (4.11)*

In Appendix A.10, we will show that equation (4.12) reduces to equation (4.11) in the absence of pressure gradients and external body forces. Equation (4.12) is

$$\Phi = -\boldsymbol{J}_1 \cdot (\nabla_T\mu_1 - \nabla_T\mu_2 - \boldsymbol{F}_1 + \boldsymbol{F}_2). \tag{A.103}$$

Assuming constant pressure and neglecting body forces, equation (A.103) may be written, using equation (2.47),

$$\Phi = -\boldsymbol{J}_1 \cdot \nabla_{T,p}\mu_1 - \boldsymbol{J}_2 \cdot \nabla_{T,p}\mu_2. \tag{A.104}$$

Using equation (2.11), equation (A.104) may be written

$$\Phi = -\rho_1 \boldsymbol{v}_1 \cdot \nabla_{T,p}\mu_1 - \rho_2 \boldsymbol{v}_2 \cdot \nabla_{T,p}\mu_2 + \boldsymbol{v} \cdot (\rho_1 \nabla_{T,p}\mu_1 + \rho_2 \nabla_{T,p}\mu_2)\,. \tag{A.105}$$

At constant temperature and pressure, the Gibbs-Duhem equation may be written, using equation (C.38),

$$\rho_1 \nabla_{T,p}\mu_1 + \rho_2 \nabla_{T,p}\mu_2 = 0\,. \tag{A.106}$$

Therefore, equation (A.105) reduces to equation (4.11):

$$\Phi = -\rho_1 \boldsymbol{v}_1 \cdot \nabla_{T,p}\mu_1 - \rho_2 \boldsymbol{v}_2 \cdot \nabla_{T,p}\mu_2\,. \tag{A.107}$$

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Appendix B: Vector and Tensor Identities

In parts of this work, we used vector or tensor identities to modify an equation. Here we show how to verify these identities, for a Cartesian coordinate system, using index notation.[1] A vector $\boldsymbol{v}$ is often represented in Cartesian coordinates by

$$\boldsymbol{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}, \tag{B.1}$$

where v_x, v_y, v_z are the component magnitudes and $\hat{i}, \hat{j}, \hat{k}$ are the unit vectors. We can alternatively represent this vector by

$$\boldsymbol{v} = v_1\hat{x}_1 + v_2\hat{x}_2 + v_3\hat{x}_3, \tag{B.2}$$

where v_1, v_2, v_3 are the components and $\hat{x}_1$, $\hat{x}_2$, $\hat{x}_3$ are the unit vectors. In index notation, we represent this vector by a summation

$$\boldsymbol{v} = \sum_i v_i\hat{x}_i, \tag{B.3}$$

where i runs from 1 to 3. Similarly, a second order tensor $\boldsymbol{T}$ can be represented in index notation by

$$\boldsymbol{T} = \sum_{i,j} T_{ij}\hat{x}_i\hat{x}_j, \tag{B.4}$$

where i and j run from 1 to 3 and $\hat{x}_i\hat{x}_j$, sometimes denoted by $\hat{x}_i \otimes \hat{x}_j$, represents the tensor product of $\hat{x}_i$ and $\hat{x}_j$.

The differential operator is, in Cartesian coordinates,

$$\nabla = \frac{\partial}{\partial x_1}\hat{x}_1 + \frac{\partial}{\partial x_2}\hat{x}_2 + \frac{\partial}{\partial x_3}\hat{x}_3, \tag{B.5}$$

and can be represented in index notation by

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[1] See pages 715-742 of **Transport Phenomena** [Bird, 1960] for an overview of index notation and its use in deriving vector and tensor identities.

$$\nabla = \sum_i \partial_i \hat{x}_i, \tag{B.6}$$

where ∂_i represents $\frac{\partial}{\partial x_i}$ and i runs from 1 to 3. Also, the substantial time derivative $\frac{D}{Dt}$ can be represented by D_t. Due to the definition of the dot product and the double dot product, several relations exist between the unit vectors [Bird, 1960, p728]:

$$\hat{x}_i \cdot \hat{x}_j = \delta_{ij}, \tag{B.7}$$

$$\hat{x}_i\hat{x}_j \cdot \hat{x}_k = \hat{x}_i\delta_{jk}, \tag{B.8}$$

$$\hat{x}_i \cdot \hat{x}_j\hat{x}_k = \delta_{ij}\hat{x}_k, \tag{B.9}$$

$$\hat{x}_i\hat{x}_j : \hat{x}_k\hat{x}_l = \delta_{il}\delta_{jk}, \tag{B.10}$$

$$\hat{x}_i\hat{x}_j \cdot \hat{x}_k\hat{x}_l = \hat{x}_i\delta_{jk}\hat{x}_l, \tag{B.11}$$

where δ_{ij} is the Kronecker delta function

$$\delta_{ij} = \begin{cases} 1, i = j \\ 0, i \neq j \end{cases}. \tag{B.12}$$

We can now verify all of the vector and tensor identities used in this work. We will present these identities next and then verify two of them -- (B.2) and (B.3). The others can be verified in a completely analogous manner.

Identity B.1

$$\nabla \cdot a\boldsymbol{v} = \boldsymbol{v} \cdot \nabla a + a\nabla \cdot \boldsymbol{v}, \tag{B.13}$$

where a is an arbitrary scalar and $\boldsymbol{v}$ is an arbitrary vector.

Identity B.2

$$\boldsymbol{v} \cdot \frac{D\boldsymbol{v}}{Dt} = \frac{D}{Dt}\frac{1}{2}\boldsymbol{v}^2, \tag{B.14}$$

where $\boldsymbol{v}$ is an arbitrary vector and $\boldsymbol{v}^2$ denotes $\boldsymbol{v} \cdot \boldsymbol{v}$.

Identity B.3

$$\nabla \cdot a\boldsymbol{U} \cdot \boldsymbol{v} = \boldsymbol{v} \cdot \nabla \cdot a\boldsymbol{U} + a\boldsymbol{U} : \nabla \boldsymbol{v}, \tag{B.15}$$

where a is an arbitrary scalar, $\boldsymbol{v}$ is an arbitrary vector and $\boldsymbol{U}$ is the unit tensor:

$$\boldsymbol{U} = \sum_{i,j} \delta_{ij} \hat{x}_i \hat{x}_j . \tag{B.16}$$

Identity B.4

$$\boldsymbol{U} : \nabla \boldsymbol{v} = \nabla \cdot \boldsymbol{v}, \tag{B.17}$$

where $\boldsymbol{v}$ is an arbitrary vector and $\boldsymbol{U}$ is the unit tensor.

Identity B.5

$$\nabla \cdot a\boldsymbol{U} = \nabla a, \tag{B.18}$$

where a is an arbitrary scalar and $\boldsymbol{U}$ is the unit tensor. We will now verify identities (B.2) and (B.3).

Verification: Identity B.2

$$\boldsymbol{v} \cdot \frac{D\boldsymbol{v}}{Dt} = \frac{D}{Dt}\frac{1}{2}\boldsymbol{v}^2, \tag{B.19}$$

where $\boldsymbol{v}$ is an arbitrary vector and $\boldsymbol{v}^2$ denotes $\boldsymbol{v} \cdot \boldsymbol{v}$. Writing the left hand side of identity (B.2) in index notation yields

$$\begin{aligned} \boldsymbol{v} \cdot \frac{D\boldsymbol{v}}{Dt} &= \sum_i v_i \hat{x}_i \cdot D_t \sum_j v_j \hat{x}_j \\ &= \sum_{i,j} v_i (\hat{x}_i \cdot \hat{x}_j) D_t v_j \\ &= \sum_i v_i D_t v_i, \end{aligned} \tag{B.20}$$

where equations (B.7) and (B.12) were used. Writing the right hand side of identity (B.2) in index notation yields

$$\frac{D}{Dt}\frac{1}{2}\boldsymbol{v}^2 = \frac{1}{2}D_t\sum_i v_i\hat{x}_i \cdot \sum_j v_j\hat{x}_j$$

$$= \sum_{i,j} D_t v_i(\hat{x}_i \cdot \hat{x}_j)v_j$$

$$= \frac{1}{2}\sum_i D_t v_i v_i, \tag{B.21}$$

where equations (B.7) and (B.12) were used. Since all of the factors in (B.21) are scalars, we can apply the chain rule:

$$\frac{1}{2}\sum_i D_t v_i v_i = \frac{1}{2}\sum_i (v_i D_t v_i + v_i D_t v_i)$$

$$= \sum_i v_i D_t v_i. \tag{B.22}$$

Comparing (B.22) with (B.20), we see that identity (B.2) is valid.

Verification: Identity B.3

$$\nabla \cdot a\boldsymbol{U} \cdot \boldsymbol{v} = \boldsymbol{v} \cdot \nabla \cdot a\boldsymbol{U} + a\boldsymbol{U}{:}\nabla\boldsymbol{v}, \tag{B.23}$$

where a is an arbitrary scalar, $\boldsymbol{v}$ is an arbitrary vector and $\boldsymbol{U}$ is the unit tensor. Writing the left hand side of identity (B.3) in index notation yields

$$\nabla \cdot a\boldsymbol{U} \cdot \boldsymbol{v} = \sum_i \partial_i\hat{x}_i \cdot a\sum_{j,k}\delta_{jk}\hat{x}_j\hat{x}_k \cdot \sum_l v_l\hat{x}_l$$

$$= \sum_i \partial_i\hat{x}_i \cdot a\sum_{j,k,l}\delta_{jk}(\hat{x}_j\hat{x}_k \cdot \hat{x}_l)v_l$$

$$= \sum_i \partial_i \hat{x}_i \cdot a \sum_j v_j \hat{x}_j,$$

$$= \sum_{i,j} \partial_i (\hat{x}_i \cdot \hat{x}_j) a v_j$$

$$= \sum_i \partial_i a v_i \tag{B.24}$$

where (B.7), (B.8) and (B.12) were used. Writing the first term on the right hand side of identity (B.3) in index notation yields

$$\boldsymbol{v} \cdot \nabla \cdot a\boldsymbol{U} = \sum_i v_i \hat{x}_i \cdot \sum_j \partial_j \hat{x}_j \cdot a \sum_{k,l} \delta_{kl} \hat{x}_k \hat{x}_l$$

$$= \sum_i v_i \hat{x}_i \cdot \sum_{j,k,l} \partial_j (\hat{x}_j \cdot \hat{x}_k \hat{x}_l) a \delta_{kl}$$

$$= \sum_i v_i \hat{x}_i \cdot \sum_j \partial_j a \hat{x}_j,$$

$$= \sum_{i,j} v_i (\hat{x}_i \cdot \hat{x}_j) \partial_j a$$

$$= \sum_i v_i \partial_i a \tag{B.25}$$

where (B.7), (B.9) and (B.12) were used. Writing the second term on the right hand side of identity (B.3) in index notation yields

$$a\boldsymbol{U} : \nabla \boldsymbol{v} = a \sum_{i,j} \delta_{ij} \hat{x}_i \hat{x}_j : \sum_k \partial_k \hat{x}_k \sum_l v_l \hat{x}_l$$

$$= a \sum_{i,j,k,l} \delta_{ij} (\hat{x}_i \hat{x}_j : \hat{x}_k \hat{x}_l) \partial_k v_l,$$

$$= \sum_i a\partial_i v_i \tag{B.26}$$

where (B.10) and (B.12) were used. Since all of the factors in (B.26) and (B.25) are scalars, we can add these two equations using the chain rule to get

$$\boldsymbol{v}\cdot\nabla\cdot a\boldsymbol{U} + a\boldsymbol{U}:\nabla\boldsymbol{v} = \sum_i v_i\partial_i a + \sum_i a\partial_i v_i$$

$$= \sum_i \partial_i a v_i. \tag{B.27}$$

Comparing (B.27) with (B.24), we see that identity (B.3) is valid.

References

Bird, R. B., W. E. Stewart and E. N. Lightfoot, Transport Phenomena, John Wiley & Sons, Inc., New York, 1960.

Appendix C: Thermodynamic Identities

In this work, we have used several thermodynamic identities or relations when deriving equations. In this appendix, we will show how all of the thermodynamic identities and relations used in this work may be derived as consequences of the postulates contained within the following two statements.[1]

1. The state of a simple thermodynamic system in equilibrium (or a mass element in local equilibrium) is completely characterized by the internal energy of the system U, the volume V and the masses M_k, (k=1,2) of the components, and there exists a continuously differentiable, invertible function of these variables called the entropy S.

2. With the intensive properties of the system (temperature, pressure, mass fractions, etc.) held constant, the entropy is a first order function of the mass of the system.

C.1 *Gibbs Relation*

From the first statement, we may write

$$S = S(U, V, M_1, M_2)\,. \tag{C.1}$$

Taking the first derivative of (C.1) yields

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,\,M_k} dU + \left(\frac{\partial S}{\partial V}\right)_{U,\,M_k} dV + \left(\frac{\partial S}{\partial M_1}\right)_{U,\,V,\,M_2} dM_1 + \left(\frac{\partial S}{\partial M_2}\right)_{U,\,V,\,M_1} dM_2\,, \tag{C.2}$$

where the subscript M_k indicates that M_1 and M_2 are held constant. The partial derivatives in equation (C.2) are well defined thermodynamical quantities:

$$\left(\frac{\partial S}{\partial U}\right)_{V,\,M_k} = \frac{1}{T}, \tag{C.3}$$

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[1] In this appendix, we will make only the postulates that allow us to derive the thermodynamic relations used in this work. For a more complete introduction to thermodynamics, see Callen [1985] or Tester and Modell [1997].

$$\left(\frac{\partial S}{\partial V}\right)_{U,\,M_k} = \frac{p}{T}, \tag{C.4}$$

$$\left(\frac{\partial S}{\partial M_1}\right)_{U,\,V,\,M_2} = -\frac{\mu_1}{T}, \tag{C.5}$$

$$\left(\frac{\partial S}{\partial M_2}\right)_{U,\,V,\,M_1} = -\frac{\mu_2}{T}, \tag{C.6}$$

where T is the temperature, p is the pressure and μ_k is the chemical potential of the k^{th} component.[2] Inserting equations (C.3) to (C.6) into equation (C.2) yields the Gibbs relation of equilibrium thermodynamics:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu_1}{T}dM_1 - \frac{\mu_2}{T}dM_2. \tag{C.7}$$

The mass M of an element in local equilibrium is constant; therefore, we may divide equation (C.7) by M to yield

$$ds = \frac{1}{T}du + \frac{p}{T}d\upsilon - \frac{\mu_1}{T}dc_1 - \frac{\mu_2}{T}dc_2, \tag{C.8}$$

where s, u, υ, c_1 and c_2 are specific quantities, defined in the main text. Note that the first derivatives appearing in equation (C.8) may be replaced by other differential operators. For example, when considering the entropy of a differential mass element in local equilibrium, we are interested in taking the substantial derivative:

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{Du}{Dt} + \frac{p}{T}\frac{D\upsilon}{Dt} - \frac{\mu_1}{T}\frac{Dc_1}{Dt} - \frac{\mu_2}{T}\frac{Dc_2}{Dt}; \tag{C.9}$$

or, we are interested in taking the gradient:

$$\nabla s = \frac{1}{T}\nabla u + \frac{p}{T}\nabla\upsilon - \frac{\mu_1}{T}\nabla c_1 - \frac{\mu_2}{T}\nabla c_2. \tag{C.10}$$

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[2] Note that the chemical potential is defined on a mass basis in this work, whereas it is usually defined on a molar basis in thermodynamics texts. Multiplying μ_k by the molar mass $\mathcal{M}_k$ of the k^{th} component yields the chemical potential as defined by Callen [1985].

The quantities T, p, μ_1 and μ_2, being partial derivatives of S, are also functions of the independent set $\{U, V, M_1, M_2\}$:

$$T = T(U, V, M_1, M_2), \tag{C.11}$$

$$p = p(U, V, M_1, M_2), \tag{C.12}$$

$$\mu_1 = \mu_1(U, V, M_1, M_2), \tag{C.13}$$

$$\mu_2 = \mu_2(U, V, M_1, M_2). \tag{C.14}$$

Assuming equations (C.11) through (C.14) are invertible, we may replace U and V in equation (C.1) with the partial derivatives T and p to yield

$$S = S(T, p, M_1, M_2). \tag{C.15}$$

Note that, if the entropy were a known function of the independent set $\{T, p, M_1, M_2\}$, it would be a partial differential equation and would require knowledge of two boundary conditions in order to contain as much information as the entropy in the form of equation (C.1). Taking the first derivative of equation (C.15) yields

$$dS = \left(\frac{\partial S}{\partial T}\right)_{p, M_k} dT + \left(\frac{\partial S}{\partial p}\right)_{T, M_k} dp + \left(\frac{\partial S}{\partial M_1}\right)_{T, p, M_2} dM_1 + \left(\frac{\partial S}{\partial M_2}\right)_{T, p, M_1} dM_2 \ . \tag{C.16}$$

The partial derivatives in equation (C.16) are, or may be related to, well defined thermodynamical quantities;

$$\left(\frac{\partial S}{\partial T}\right)_{p, M_k} = \frac{C_p}{T}, \tag{C.17}$$

$$\left(\frac{\partial S}{\partial M_1}\right)_{T, p, M_2} = s_1, \tag{C.18}$$

$$\left(\frac{\partial S}{\partial M_2}\right)_{T, p, M_1} = s_2, \tag{C.19}$$

where C_p is the heat capacity at constant pressure and s_k is the partial specific entropy of the k^{th} component. We can relate the partial derivative $\left(\frac{\partial S}{\partial p}\right)_{T,\,M_k}$ to the coefficient of thermal expansion α_p,

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\,M_k}, \tag{C.20}$$

by studying the sum $U + pV - TS$, called the Gibbs free energy G:

$$G = U + pV - TS. \tag{C.21}$$

Taking the first derivative of (C.21) yields

$$dG = dU + pdV + Vdp - TdS - SdT. \tag{C.22}$$

Combining equation (C.22) with the Gibbs relation, equation (C.7), yields

$$dG = -SdT + Vdp + \mu_1 dM_1 + \mu_2 dM_2. \tag{C.23}$$

Now we may use equation (C.23) to get

$$\left(\frac{\partial S}{\partial p}\right)_{T,\,M_k} = \left(\frac{\partial}{\partial p}\right)_{T,\,M_k}\left(-\frac{\partial G}{\partial T}\right)_{p,\,M_k} = -\left(\frac{\partial}{\partial T}\right)_{p,\,M_k}\left(\frac{\partial G}{\partial p}\right)_{T,\,M_k} = -\left(\frac{\partial V}{\partial T}\right)_{p,\,M_k}. \tag{C.24}$$

Combining equations (C.20) and (C.24) yields

$$\left(\frac{\partial S}{\partial p}\right)_{T,\,M_k} = -V\alpha_p. \tag{C.25}$$

Combining equations (C.25), (C.19), (C.18) and (C.17) with equation (C.16) yields an expression analogous to the Gibbs relation:

$$dS = \frac{C_p}{T}dT - V\alpha_p dp + s_1 dM_1 + s_2 dM_2. \tag{C.26}$$

For a binary mass element in local equilibrium, equation (C.26) may be written in terms of the substantial derivative to yield, after dividing by M,

$$\frac{Ds}{Dt} = \frac{c_p}{T}\frac{DT}{Dt} - \frac{\alpha_p}{\rho}\frac{Dp}{Dt} + s_1\frac{Dc_1}{Dt} + s_2\frac{Dc_2}{Dt}, \tag{C.27}$$

where c_p is the heat capacity per unit mass and ρ is the density of the system.

C.2 *Gibbs-Duhem Relation*

In order to derive the Gibbs-Duhem relation, we will study the second statement: "With the intensive properties of the system (T, p, c_1, c_2, *etc.*) held constant, the entropy is a first order function of the mass of the system." Mathematically, this statement means, for the independent set $\{T, p, M_1, M_2\}$,

$$S(T, p, \lambda M_1, \lambda M_2) = \lambda S(T, p, M_1, M_2); \tag{C.28}$$

or,

$$S' = \lambda S, \tag{C.29}$$

where λ is an arbitrary constant and

$$S' = S(T, p, \lambda M_1, \lambda M_2). \tag{C.30}$$

Alternatively, we may use the set $\{U, V, M_1, M_2\}$ and write, noting that with the intensive variables held constant, U and V will be first order functions of the mass as well,

$$S' = \lambda S, \tag{C.31}$$

where

$$S' = S(\lambda U, \lambda V, \lambda M_1, \lambda M_2). \tag{C.32}$$

Taking the first derivative of equation (C.31) with respect to λ yields, in light of (C.32),

$$\left(\frac{\partial S}{\partial \lambda U}\right)_{V,\,M_k}\frac{d\lambda U}{d\lambda}+\left(\frac{\partial S}{\partial \lambda V}\right)_{U,\,M_k}\frac{d\lambda V}{d\lambda}+\left(\frac{\partial S}{\partial \lambda M_1}\right)_{U,\,V,\,M_2}\frac{d\lambda M_1}{d\lambda}$$

$$+\left(\frac{\partial S}{\partial \lambda M_2}\right)_{U,\,V,\,M_1}\frac{d\lambda M_2}{d\lambda} = \frac{d\lambda S}{d\lambda};\text{(C.33)}$$

or,

$$\left(\frac{\partial S}{\partial \lambda U}\right)_{V,\,M_k}U+\left(\frac{\partial S}{\partial \lambda V}\right)_{U,\,M_k}V+\left(\frac{\partial S}{\partial \lambda M_1}\right)_{U,\,V,\,M_2}M_1+\left(\frac{\partial S}{\partial \lambda M_2}\right)_{U,\,V,\,M_1}M_2 = S. \quad \text{(C.34)}$$

Since λ is arbitrary, we may let $\lambda = 1$ and use equations (C.31), (C.3), (C.4), (C.5) and (C.6) to yield the Euler relation of equilibrium thermodynamics:[3]

$$S = \frac{1}{T}U+\frac{p}{T}V-\frac{\mu_1}{T}M_1-\frac{\mu_2}{T}M_2. \quad \text{(C.35)}$$

Multiplying (C.35) by T and taking the first derivative yields

$$TdS+SdT = dU+pdV+Vdp-\mu_1 dM_1-M_1 d\mu_1-\mu_2 dM_2-M_2 d\mu_2. \quad \text{(C.36)}$$

Combining equation (C.36) with equation (C.7) yields the Gibbs-Duhem relation of equilibrium thermodynamics

$$SdT-Vdp+M_1 d\mu_1+M_2 d\mu_2 = 0. \quad \text{(C.37)}$$

For a mass element in local equilibrium, equation (C.37) may be written in terms of the gradient operator to yield, after dividing by V,

$$\rho s\nabla T-\nabla p+\rho_1\nabla\mu_1+\rho_2\nabla\mu_2 = 0. \quad \text{(C.38)}$$

In an analogous manner, we may take the first derivative of equation (C.29) to yield, in light of (C.30),

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[3] Equation (C.35) may also be obtained by integrating equation (C.7), the Gibbs relation, from $\{S, U, V, M_1, M_2\}$ to $\{\lambda S, \lambda U, \lambda V, \lambda M_1, \lambda M_2\}$ while holding $\{T, p, \mu_1, \mu_2\}$ constant.

$$\left(\frac{\partial S}{\partial T}\right)_{p,\,M_k}\left(\frac{dT}{d\lambda}\right)+\left(\frac{\partial S}{\partial p}\right)_{T,\,M_k}\left(\frac{dp}{d\lambda}\right)$$

$$+\left(\frac{\partial S}{\partial \lambda M_1}\right)_{T,\,p,\,M_2}\left(\frac{d\lambda M_1}{d\lambda}\right)+\left(\frac{\partial S}{\partial \lambda M_2}\right)_{T,\,p,\,M_1}\left(\frac{d\lambda M_2}{d\lambda}\right) = \frac{d\lambda S}{d\lambda};\text{(C.39)}$$

or, since $\frac{dT}{d\lambda} = 0$ and $\frac{dp}{d\lambda} = 0$ because T and p are being held constant,

$$\left(\frac{\partial S}{\partial \lambda M_1}\right)_{T,\,p,\,M_2} M_1+\left(\frac{\partial S}{\partial \lambda M_2}\right)_{T,\,p,\,M_1} M_2 = S. \qquad \text{(C.40)}$$

Since λ may be any number, we may let $\lambda = 1$ and use equations (C.29), (C.18) and (C.19) to yield a relation analogous to the Euler relation[4]:

$$S = s_1 M_1 + s_2 M_2. \qquad \text{(C.41)}$$

Taking the first derivative of equation (C.41) yields

$$dS = s_1 dM_1 + M_1 ds_1 + s_2 dM_2 + M_2 ds_2. \qquad \text{(C.42)}$$

Combining equations (C.42) and (C.26) yields an equation analogous to the Gibbs-Duhem relation:

$$\frac{C_p}{T}dT - V\alpha_p dp - M_1 ds_1 - M_2 ds_2 = 0. \qquad \text{(C.43)}$$

For a mass element in local equilibrium, equation (C.43) may be written in terms of the gradient operator to yield, after dividing by V,

$$\rho\frac{c_p}{T}\nabla T - \alpha_p \nabla p - \rho_1 \nabla s_1 - \rho_2 \nabla s_2 = 0. \qquad \text{(C.44)}$$

In order to derive the rest of the relations used in this work, we will first reiterate the statements made at the beginning of the appendix in a more general manner, following the development of Tester and Modell [1997].

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[4] Equation (C.41) may also be obtained by integrating equation (C.26) from $\{S, T, p, M_1, M_2\}$ to $\{\lambda S, T, p, \lambda M_1, \lambda M_2\}$ while holding $\{T, p, s_1, s_2\}$ constant.

1. "The state of a stable, single phase, [n-component] system can be specified as a continuous function of $n+2$ variables. . . . We are completely free to select these $n+2$ independent variables from a large set of intensive and extensive properties." Any extensive variable B or intensive variable b may be written as a continuously differentiable, invertible function of the $n+2$ independent variables [Tester, 1997, p318].

2. With the intensive properties of the system (b, T, p, c_1, c_2, *etc.*) held constant, B is a first order function of the mass of the system [Tester, 1997, p320].

As an example, in light of the first statement, we may choose $\{T, p, M_1, M_2\}$ as our independent set of variables and write, for any extensive variable B of a binary system,

$$B = B(T, p, M_1, M_2), \tag{C.45}$$

or, for any intensive variable b,

$$b = b(T, p, M_1, M_2). \tag{C.46}$$

In light of the second statement, we may write

$$B(T, p, \lambda M_1, \lambda M_2) = \lambda B(T, p, M_1, M_2), \tag{C.47}$$

where λ is an arbitrary constant. Alternatively, we may choose $\{T, p, c_1, M\}$ as our independent set and write, in light of the first statement,

$$B = B(T, p, c_1, M), \tag{C.48}$$

and

$$b = b(T, p, c_1, M). \tag{C.49}$$

Further, since b is intensive, we may write

$$b(T, p, c_1, \lambda M) = b(T, p, c_1, M). \tag{C.50}$$

Equations (C.45), (C.48) and (C.49) are equivalent to equations (9-4), (9-5) and (9-7), respectively, of **Thermodynamics and Its Applications** [Tester, 1997]. The only difference is that Tester and Modell denote extensive variables by $\underline{B}$ and intensive variables by B; also, they use moles and mole fractions rather than masses and mass fractions.

C.3 *Partial Specific Volume*

Let us choose $B = V$. Then we may write, in light of (C.45),

$$V = V(T, p, M_1, M_2), \tag{C.51}$$

and

$$V(T, p, \lambda M_1, \lambda M_2) = \lambda V(T, p, M_1, M_2). \tag{C.52}$$

We may take the first derivative of (C.52) with respect to λ and then set $\lambda = 1$ as before to get

$$V = \upsilon_1 M_1 + \upsilon_2 M_2, \tag{C.53}$$

where υ_1 and υ_2 are partial specific volumes:

$$\upsilon_1 = \left(\frac{\partial V}{\partial M_1}\right)_{T, p, M_2}, \tag{C.54}$$

$$\upsilon_2 = \left(\frac{\partial V}{\partial M_2}\right)_{T, p, M_1}. \tag{C.55}$$

Dividing equation (C.53) by the volume V of a mass element in local equilibrium yields

$$\rho_1 \upsilon_1 + \rho_2 \upsilon_2 = 1. \tag{C.56}$$

C.4 *Chemical Potential*

Let us choose $b = \mu_1$. Then we may write, in light of equations (C.49) and (C.50),

$$\mu_1 = \mu_1(T, p, c_1, M) \tag{C.57}$$

and

$$\mu_1(T, p, c_1, \lambda M) = \mu_1(T, p, c_1, M). \tag{C.58}$$

We may take the first derivative of (C.58) with respect to λ and then set $\lambda = 1$ as before to yield

$$\left(\frac{\partial \mu_1}{\partial M}\right)_{T,\,p,\,c_1} M = 0; \tag{C.59}$$

or, since M is not zero in general,

$$\left(\frac{\partial \mu_1}{\partial M}\right)_{T,\,p,\,c_1} = 0. \tag{C.60}$$

Taking the first derivative of equation (C.57) yields, using (C.60),[5]

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_{p,\,c_1} dT + \left(\frac{\partial \mu_1}{\partial p}\right)_{T,\,c_1} dp + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} dc_1. \tag{C.61}$$

If c_1 and M are both constant in a binary system, then the masses M_1 and M_2 are constant and equation (C.61) may be written

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_{p,\,M_k} dT + \left(\frac{\partial \mu_1}{\partial p}\right)_{T,\,M_k} dp + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} dc_1. \tag{C.62}$$

The first two partial derivatives in equation (C.62) may be replaced by more well defined thermodynamical quantities by using equation (C.23), along with equations (C.18) and (C.54):

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{p,\,M_k} = -s_1, \tag{C.63}$$

$$\left(\frac{\partial \mu_1}{\partial p}\right)_{T,\,M_k} = \upsilon_1. \tag{C.64}$$

Inserting equations (C.63) and (C.64) into (C.62) yields

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[5] Note that the partial derivatives appearing in (C.61) should contain the subscript M: $d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_{p,\,c_1,\,M} dT + \left(\frac{\partial \mu_1}{\partial p}\right)_{T,\,c_1,\,M} dp + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p,\,M} dc_1$. However, since intensive variables are independent of the mass of the system, the mass need not be considered constant and we have neglected the subscript M in equation (C.61) and throughout the rest of this appendix.

$$d\mu_1 = -s_1 dT + \upsilon_1 dp + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} dc_1 . \tag{C.65}$$

For a binary mass element in local equilibrium, equation (C.65) may be written in terms of the gradient operator to yield

$$\nabla \mu_1 = -s_1 \nabla T + \upsilon_1 \nabla p + \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} \nabla c_1 . \tag{C.66}$$

C.5 Partial Specific Entropy

Let us choose $b = s_1$. Then we may write, in light of (C.49),

$$s_1 = s_1(T, p, c_1, M) . \tag{C.67}$$

The first derivative of equation (C.67) may be written, analogously to equation (C.62),

$$ds_1 = \left(\frac{\partial s_1}{\partial T}\right)_{p, M_k} dT + \left(\frac{\partial s_1}{\partial p}\right)_{T, M_k} dp + \left(\frac{\partial s_1}{\partial c_1}\right)_{T,p} ds_1 . \tag{C.68}$$

Let us write the partial derivatives appearing in (C.68) in more useful forms. Using equation (C.26) we may write

$$\left(\frac{\partial s_1}{\partial T}\right)_{p, M_k} = \left(\frac{\partial}{\partial T}\right)_{p, M_k}\left(\frac{\partial S}{\partial M_1}\right)_{T, p, M_2} = \left(\frac{\partial}{\partial M_1}\right)_{T, p, M_2}\left(\frac{\partial S}{\partial T}\right)_{p, M_k} = \frac{1}{T}\left(\frac{\partial C_p}{\partial M_1}\right)_{T, p, M_2} \tag{C.69}$$

Similarly, using (C.26), (C.20) and (C.54),

$$\left(\frac{\partial s_1}{\partial p}\right)_{T, M_k} = -\left(\frac{\partial V\alpha_p}{\partial M_1}\right)_{T, p, M_2} = -\left(\frac{\partial \upsilon_1}{\partial T}\right)_{p, M_k} . \tag{C.70}$$

Using equation (C.63) we may write

$$\left(\frac{\partial s_1}{\partial c_1}\right)_{T,p} = -\left(\frac{\partial}{\partial c_1}\right)_{T,p}\left(\frac{\partial \mu_1}{\partial T}\right)_{p, M_k} = -\left(\frac{\partial}{\partial T}\right)_{p, M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} . \tag{C.71}$$

Inserting equations (C.71), (C.70) and (C.69) into (C.68) yields

$$ds_1 = \frac{1}{T}\left(\frac{\partial C_p}{\partial M_1}\right)_{T, p, M_2} dT - \left(\frac{\partial \upsilon_1}{\partial T}\right)_{p, M_k} dp - \left(\frac{\partial}{\partial T}\right)_{p, M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p} dc_1 . \tag{C.72}$$

For a binary mass element in local equilibrium, equation (C.72) may be written in terms of the gradient operator to yield

$$\nabla s_1 = \frac{1}{T}\left(\frac{\partial c_p}{\partial c_1}\right)_{T,p,M_2}\nabla T - \left(\frac{\partial \upsilon_1}{\partial T}\right)_{p,M_k}\nabla p - \left(\frac{\partial}{\partial T}\right)_{p,M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,p}\nabla c_1 . \qquad \text{(C.73)}$$

C.6 *Enthalpy and Partial Specific Enthalpy*

Let us define a function H, called the enthalpy, by the relation

$$H = U + pV. \qquad \text{(C.74)}$$

Taking the first derivative of (C.74), and using equation (C.7) to eliminate dU, yields

$$dH = TdS + Vdp + \mu_1 dM_1 + \mu_2 dM_2 . \qquad \text{(C.75)}$$

Taking the partial derivative of equation (C.75) with respect to M_k, at constant T, p and $M_{j,j\neq k}$, yields, using equation (C.18),

$$h_k = Ts_k + \mu_k , \quad (k = 1,2), \qquad \text{(C.76)}$$

where h_k is the partial specific enthalpy of the k^{th} component:

$$h_k = \left(\frac{\partial H}{\partial M_k}\right)_{T,p,M_j}, \quad (k = 1,2), \ (j \neq k). \qquad \text{(C.77)}$$

Let us choose $B = H$. Then we may write, in light of equations (C.45) and (C.47),

$$H = H(T, p, M_1, M_2), \qquad \text{(C.78)}$$

and

$$H(T, p, \lambda M_1, \lambda M_2) = \lambda H(T, p, M_1, M_2). \qquad \text{(C.79)}$$

We may take the first derivative of (C.79) with respect to λ and then set $\lambda = 1$ as before to obtain an Euler relation for H:

$$H = h_1 M_1 + h_2 M_2 . \qquad \text{(C.80)}$$

Let us obtain a Gibbs relation and a Gibbs-Duhem relation for H. Taking the first derivative of (C.78) yields

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,\,M_k} dT + \left(\frac{\partial H}{\partial p}\right)_{T,\,M_k} dp + \left(\frac{\partial H}{\partial M_1}\right)_{T,\,p,\,M_2} dM_1 + \left(\frac{\partial H}{\partial M_2}\right)_{T,\,p,\,M_1} dM_2. \quad \text{(C.81)}$$

We may obtain the partial derivative $\left(\frac{\partial H}{\partial T}\right)_{p,\,M_k}$ by using equations (C.75) and (C.17):

$$\left(\frac{\partial H}{\partial T}\right)_{p,\,M_k} = T\left(\frac{\partial S}{\partial T}\right)_{p,\,M_k} = C_p. \quad \text{(C.82)}$$

We may obtain the partial derivative $\left(\frac{\partial H}{\partial p}\right)_{T,\,M_k}$ by using equations (C.75) and (C.25):

$$\left(\frac{\partial H}{\partial p}\right)_{T,\,M_k} = T\left(\frac{\partial S}{\partial p}\right)_{T,\,M_k} + V = -TV\alpha_p + V. \quad \text{(C.83)}$$

Inserting equations (C.77), (C.82) and (C.83) into equation (C.81) yields a Gibbs relation for H:

$$dH = C_p dT + V(1 - T\alpha_p)dp + h_1 dM_1 + h_2 dM_2. \quad \text{(C.84)}$$

Taking the first derivative of (C.80) yields

$$dH = h_1 dM_1 + M_1 dh_1 + h_2 dM_2 + M_2 dh_2. \quad \text{(C.85)}$$

Combining (C.85) and (C.84) yields a Gibbs-Duhem relation for H:

$$C_p dT + V(1 - T\alpha_p)dp - M_1 dh_1 - M_2 dh_2 = 0. \quad \text{(C.86)}$$

For a mass element in local equilibrium, equation (C.86) can be written in terms of the gradient operator to yield, after dividing by V,

$$\rho c_p \nabla T + (1 - T\alpha_p)\nabla p - \rho_1 \nabla h_1 - \rho_2 \nabla h_2 = 0. \quad \text{(C.87)}$$

Let us choose $b = h_1$. Then we may write, in light of (C.49),

$$h_1 = h_1(T, p, c_1, M). \quad \text{(C.88)}$$

The first derivative of equation (C.88) may be written, analogously to equation (C.62),

$$dh_1 = \left(\frac{\partial h_1}{\partial T}\right)_{p,\,M_k} dT + \left(\frac{\partial h_1}{\partial p}\right)_{T,\,M_k} dp + \left(\frac{\partial h_1}{\partial c_1}\right)_{T,\,p} dc_1 . \tag{C.89}$$

Let us write the partial derivatives appearing in (C.89) in more useful forms. Using equation (C.84) we may write

$$\left(\frac{\partial h_1}{\partial T}\right)_{p,\,M_k} = \left(\frac{\partial}{\partial T}\right)_{p,\,M_k}\left(\frac{\partial H}{\partial M_1}\right)_{T,\,p,\,M_2} = \left(\frac{\partial}{\partial M_1}\right)_{T,\,p,\,M_2}\left(\frac{\partial H}{\partial T}\right)_{p,\,M_k} = \left(\frac{\partial C_p}{\partial M_1}\right)_{T,\,p,\,M_2} \tag{C.90}$$

Using (C.76), (C.70) and (C.64), we may write

$$\left(\frac{\partial h_1}{\partial p}\right)_{T,\,M_k} = \upsilon_1 - T\left(\frac{\partial \upsilon_1}{\partial T}\right)_{p,\,M_k} . \tag{C.91}$$

Similarly, we may use (C.76) and (C.71) to write

$$\left(\frac{\partial h_1}{\partial c_1}\right)_{T,\,p} = \left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} - T\left(\frac{\partial}{\partial T}\right)_{p,\,M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} . \tag{C.92}$$

Inserting equations (C.92), (C.91) and (C.90) into (C.89) yields

$$dh_1 = c_{p_1} dT + \left[\upsilon_1 - T\left(\frac{\partial \upsilon_1}{\partial T}\right)_{p,\,M_k}\right] dp + \left[\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} - T\left(\frac{\partial}{\partial T}\right)_{p,\,M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p}\right] dc_1 , \tag{C.93}$$

where c_{p_1} is the partial specific heat capacity:

$$c_{p_1} = \left(\frac{\partial c_p}{\partial M_1}\right)_{T,\,p,\,M_2} . \tag{C.94}$$

For a binary mass element in local equilibrium, equation (C.93) may be written in terms of the gradient operator to yield

$$\nabla h_1 = c_{p_1} \nabla T + \left[\upsilon_1 - T\left(\frac{\partial \upsilon_1}{\partial T}\right)_{p,\,M_k}\right] \nabla p$$

$$+ \left[\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p} - T\left(\frac{\partial}{\partial T}\right)_{p,\,M_k}\left(\frac{\partial \mu_1}{\partial c_1}\right)_{T,\,p}\right] \nabla c_1 . \tag{C.95}$$

C.7 *Osmotic Pressure*

Considering a binary solution in which component 1 is the solvent, let us define a function π, called the osmotic pressure, by the relation

$$d\mu_1 = \upsilon_1 dp - \upsilon_1 d\pi . \qquad \text{(C.96)}$$

Comparing equation (C.96) with (C.65), we see that π is, in general, a function of temperature and concentration. Note that at equilibrium in an osmotic pressure experiment, π becomes equal to the pressure difference between two sides of a semipermeable membrane that is separating the solution on one side from pure solvent on the other [Katchalsky, 1965, p54]. In the most general case, π may be thought of as a function of temperature and concentration defined by equation (C.96). For a binary mass element in local equilibrium, equation (C.96) may be written in terms of the gradient operator to yield

$$\nabla\mu_1 = \upsilon_1 \nabla p - \upsilon_1 \nabla\pi . \qquad \text{(C.97)}$$

All of the thermodynamic identities and relations used in this work have now been derived.

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